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COMPARISON OF NATURAL AGING OF PAPER WITH ACCELERATED AGING BY HEATING

By Royal H. Rasch[1] and B. W. Scribner

ABSTRACT

Thirty-three papers ranging in fiber composition from 100 percent rag to 100 percent sulphite, including purified wood fiber papers, and book papers prepared from mixtures of sulphite and soda pulp, were tested after 4 years of normal aging for chemical purity and strength. The chemical properties of the papers showed little change under the tests applied. The folding endurance of the papers, however, underwent marked changes, several decreasing to less than half of the initial figure. The papers were placed in approximately the same order of stability by normal aging as they were by the accelerated aging tests (72 hours at 100° C.) conducted 4 years previously. This constitutes additional evidence of the validity of the heat test as a means of estimating the relative aging quality of papers.

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I. INTRODUCTION

In 1928 study was made at the Bureau of Standards of a series of 37 commercial papers with particular reference to chemical purity, strength, and relative permanence as estimated by an accelerated aging test. The portion of this study already published deals principally with the physical properties of the papers and the extent of their alteration under accelerated aging.[2] The papers included in the study were, for the most part, writing papers ranging in fiber furnish from 100 percent sulphite to 100 percent rag. Four papers prepared from wood fibers of high chemical purity, and 5 book papers made from mixtures of sulphite and soda pulp were included.

Retests have been made recently of 33 of the papers for strength, alpha cellulose content, copper number, and acidity, after having been stored for 4 years. It is the purpose of this article to indicate briefly the changes, particularly in folding endurance, which have occurred during this relatively short period of normal aging in relation to the initial characteristics of the papers, and to the results of the accelerated aging tests made 4 years previously.

The papers were stored in a tightly closed bookcase in an office room free from abnormal atmospheric conditions, and each test sample was kept enclosed in a separate envelope, in order to minimize

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[2] R. H. Rasch, A Study of Purified Wood Fibers as a Paper-Making Material, B.S. Jour. Research, vol. 3 (RP107), p. 469, 1929.

any possible effect of external deteriorative influences. The data on alpha cellulose content, copper number, and acidity contained in this article were, for the most part, not included in the previous article which this supplements.

II. TEST METHODS

In testing the papers, the official methods of the Technical Association of the Pulp and Paper Industry were used for the determination of weight, bursting strength, thickness, folding endurance, breaking load, tearing strength, ash, resin, and glue.[3] The procedure for the determination of alpha cellulose content and copper number have been described in a previous publication.[4] Determinations of titratable acidity were made by the Kohler-Hall method, but the acidity is expressed as percent sulphuric anhydride rather than as acid number.[5] The accelerated aging or stability test used consists in exposing the paper specimen under test to a current of air at 100° C. for 72 hours and then determining to what extent the paper has been altered in its properties. This test has been described in previous publications.[6]

III. RESULTS

The test results are given in table 1, which also contains descriptions of the papers and the more important original test data. For additional information on the characteristics of the papers, the reader is referred to the previous publication.[7] In a few cases complete tests were not made. Four years of normal aging resulted in decreases in the folding endurance of most of the papers, which were quite large for many of them, some decrease in tearing strength and bursting strength for the least stable papers, and no appreciable change in the breaking load of any of the papers. The acidity increased slightly in most cases, the greatest changes being recorded for the sulphite bond and sulphite-soda book papers. The copper numbers of the papers were unaltered within the limits of experimental error. The alpha cellulose contents of the sulphite bond papers and two of the sulphite-rag papers underwent slight decreases. Similar changes in the various properties were obtained with the 72-hour heat treatment at 100° C., except that this treatment had a uniformly greater deteriorative effect. It caused decreases in alpha cellulose content and increases in copper number, which in most instances did not take place under normal aging for 4 years.

The results of normal aging bear out the heat tests in showing that the folding endurance is the most sensitive of the tests here discussed for indicating the relative stabilities of the papers.

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[3] Paper Testing Methods, prepared by the Committee on Paper Testing of the Technical Association of the Pulp and Paper Industry, Lockwood Trade Jour. Co., New York, 1929.

[4] Burton, J. O., and Rasch, R. H., The Determination of the Alpha Cellulose Content and Copper Number of Paper, B.S.Jour. Research, vol. 6 (RP295), p. 603, 1931.

[5] Kohler, S., and Hall, G., Acidity in Paper, Paper Industry, vol. 7, no. 7, p. 1, 1925.

[6] Rasch, R. H., Accelerated Aging Test for Paper, B.S.Jour. Research, vol. 7 (RP352), p. 465, 1931. See also footnote 2, p. 727.

[7] See footnote 2, p. 727.

TABLE 1.—*Test data on papers*

ALL-RAG PAPERS

Sample number	Kind of fiber: Rag	Kind of fiber: Chemical wood: Coniferous	Kind of fiber: Chemical wood: Deciduous	Kind of sizing	Folding endurance: Machine direction	Folding endurance: Cross direction	Ash	Rosin	Glue	Acidity[1] (Kohler-Hall): Total	Acidity[1] (Kohler-Hall): External	Acidity[1] (Kohler-Hall): Internal	Alpha cellulose content	Copper number	Tests after heating at 100° C. for 72 hours: Bursting strength in percent of initial	Tests after heating at 100° C. for 72 hours: Folding endurance in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Tensile strength in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Tearing strength in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Increase in acidity	Tests after heating at 100° C. for 72 hours: Decrease in alpha cellulose in percent of initial	Tests after heating at 100° C. for 72 hours: Increase in copper number	Tests after 4 years normal aging: Bursting strength in percent of initial	Tests after 4 years normal aging: Folding endurance in percent of initial[2]	Tests after 4 years normal aging: Tensile strength in percent of initial[2]	Tests after 4 years normal aging: Tearing strength in percent of initial[2]	Tests after 4 years normal aging: Increase in acidity	Tests after 4 years normal aging: Decrease in alpha cellulose in percent of initial	Tests after 4 years normal aging: Increase in copper number
	Pct.	*Pct.*	*Pct.*		*Double folds*	*Double folds*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*															
104	90	10	0	Rosin and glue	1,900	1,100	1.15	1.9	7.7	0.078	0.040	0.038	92.9	1.61	98	61	102	97	89	0.069	1.3	0.22									
113	100	0	0	do	3,900	5,600	.51	1.5	2.5	.078	.040	.038	92.9	1.61	95	60	97	89	.069	1.3	.22									
114	100	0	0	Rosin	1,700	440	.10	1.4		.014			90.0	.30	111	79	105	94	.000	1.0	.08	100	94	105	100	0.000	0	.11
118	100	0	0	Rosin and glue	4,700	6,200	.60	1.6	4.7	.169	.062	.077	95.1	.88	90	55	97	77	.016	6.0	.04	100	106	106	91	.000	0	
119	100	0	0	Rosin	2,600	1,700	.54	2.4		.086			92.9	1.25	98	22	98	63	.043	6.0	.46	100	65	101	93	.010	0	.03
120	100	0	0	Rosin and glue	3,600	2,800	.73	1.4	2.2	.090	.043	.047	94.4	1.11	95	82	94	82	.042	1.4	.26	106	105	105	90	.011	0	
127	100	0	0	Rosin	1,300	1,200	.75	2.2		.138			91.1	.93	70	70	82	80	.045	3.4	.78	92	101	106	106	.000	0	
126	100	0	0	Rosin and glue	3,000	1,900	.80	2.3	4.6	.235	.122	.113	94.4	1.23	99	77	101	90	.046	2.2	.39	101	80	97	100	.000	0	
129	100	0	0	Rosin	3,100	2,600	.71	2.4		.120			92.2	1.03	107	58	106	73	.060	5.6	.61	99	104	99	100	.000	0	
128	100	0	0	Rosin and glue	3,500	2,600	.77	2.5	3.5	.218	.114	.104	94.3	1.12	92	69	102	88	.039	2.6	.16	95	85	105	102	.016	0	
131	100	0	0	Rosin	9		.82	1.7		.075			83.9	2.20	94	63	106	103	.056	5.7	.52	94	86	108	105	.000	0	
130	100	0	0	Rosin and glue	22	20	.72	1.5	3.4	.084	.022	.062	86.6	2.43	96	53	106	103	.048	2.6	.23	92	93	105	104	.022	.2	.05
				PART RAG PAPERS																								
111	60	40	0	Rosin	102	71	0.48	2.7		0.076			82.0	3.24	90	24	97	73	0.051	7.8	0.57	96	63	100	80	.017	1.6	0
112	60	40	0	Rosin and glue	210	110	.52	2.5	1.1	.119	0.040	.079	81.3	.39	84	16	93	74	.043	6.3	.42	98	56	104	90	.000	1.7	0
133	65	35	0	Rosin	340	190	.39	1.6		.055			79.0	2.31	85	15	92	77	.049	5.7	1.50	88	59	93	88	.017	0	.09
132	65	35	0	Rosin and glue	340	220	.43	1.5	1.1	.079	.031	.048	80.2	3.38	85	17	93	81	.047	4.7	.53	77	66	94	98	.000	.5	

[1] Acid calculated as percent SO

Average of machine and cross directions.

TABLE 1.—*Test data on papers*—Continued

PURIFIED WOOD FIBER PAPERS

Sample number	Kind of fiber: Rag	Kind of fiber: Chemical wood: Coniferous	Kind of fiber: Chemical wood: Deciduous	Kind of sizing	Folding endurance: Machine direction	Folding endurance: Cross direction	Ash	Rosin	Glue	Acidity[1] (Kohler-Hall): Total	Acidity[1] (Kohler-Hall): External	Acidity[1] (Kohler-Hall): Internal	Alpha cellulose content	Copper number	Tests after heating at 100° C. for 72 hours: Bursting strength in percent of initial	Tests after heating at 100° C. for 72 hours: Folding endurance in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Tensile strength in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Tearing strength in percent of initial[2]	Tests after heating at 100° C. for 72 hours: Increase in acidity	Tests after heating at 100° C. for 72 hours: Decrease in alpha cellulose in percent of initial	Tests after heating at 100° C. for 72 hours: Increase in copper number	Tests after 4 years normal aging: Bursting strength in percent of initial	Tests after 4 years normal aging: Folding endurance in percent of initial[2]	Tests after 4 years normal aging: Tensile strength in percent of initial[2]	Tests after 4 years normal aging: Tearing strength in percent of initial[2]	Tests after 4 years normal aging: Increase in acidity	Tests after 4 years normal aging: Decrease in alpha cellulose in percent of initial	Tests after 4 years normal aging: Increase in copper number
	Pct.	*Pct.*	*Pct.*		*Double folds*	*Double folds*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*															
105	0	100	0	Rosin and glue	1,400	800	0.34	1.4	2.7	0.092	0.046	0.046	90.5	1.40	99	54	100	82	0.050	1.1	0.32	100	58	100	88	0.000	0	0.06
106	0	100	0	do	2,500	1,600	.51	1.5	2.4	.063	.028	.035	88.8	1.37	92	71	100	94	.031	1.9	.35	99	79	102	95	.001	0	.11
107	0	100	0	do	1,900	1,200	.39	1.2	2.2	.114	.081	.033	88.3	1.78	98	56	103	81	.028	1.9	.20	91	79	107	83	.000	0	0
122	0	100	0	Unsized	69	7	.15	.1	----	----	----	---	92.2	1.02	100	104	106	93	-----	1.3	.12	100	89	103	100	-----	-----	-----
SULPHITE WOOD FIBER PAPERS																												
108	0	100	0	Rosin	15	17	7.12	2.2	----	0.108	----	----	77.8	4.89	80	10	110	73	0.056	5.7	0.46	82	45	92	78	0.037	2.6	0
109	0	100	0	do	49	22	1.06	2.4	----	.084	----	----	77.2	4.78	74	9	100	66	.071	4.1	.49	88	35	104	85	.033	1.9	0
110	0	100	0	do	530	250	.60	2.8	----	.113	----	----	81.6	3.77	70	1	87	52	.014	5.9	.55	90	36	100	78	.024	1.6	0
115	0	100	0	do	140	130	2.61	1.3	----	.058	----	----	80.5	3.08	83	15	89	70	.018	3.5	.63	-----	52	-----	----	----	2.0	-----
116	0	100	0	do	500	360	.51	1.9	----	.119	----	----	76.4	4.27	79	3	97	58	.075	7.9	.51	87	21	98	78	.000	1.7	-----
117	0	100	0	do	150	160	2.92	1.4	----	.033	----	----	80.6	2.98	82	12	92	77	.023	4.3	.59	89	62	100	85	.030	1.2	-----
134	0	100	0	do	510	190	.48	1.7	----	.082	----	----	79.9	3.75	73	1	81	45	.058	4.1	.36	85	56	95	85	.034	.7	-----
135	0	100	0	do	110	72	6.12	2.0	----	.066	----	----	79.2	3.29	86	6	95	71	.031	4.1	.80	88	40	105	93	.032	-----	-----
SODA-SULPHITE WOOD FIBER PAPERS																												
123	0	65	35	Rosin	5	4	19.11	0.6	----	0.085	----	----	74.0	3.72	94	35	101	82	0.072	6.8	0.40	75	75	108	78	0.032	-----	-----
124	0	50	50	do	2	2	19.99	.8	----	.095	----	----	63.8	5.19	95	48	95	87	.067	8.4	.19	90	79	102	71	.033	0	0.12
147	0	35	65	do	16	6	17.25	.6	----	.038	----	----	77.9	2.29	94	64	96	103	.010	.2	.06	88	73	96	103	.011	0	0
148	0	25	75	do	15	8	5.04	1.9	----	.069	----	----	81.0	3.17	97	37	98	73	.057	4.5	.45	100	67	90	83	.055	0	-----
152	0	25	75	do	9	7	15.55	1.1	----	.031	----	----	78.8	2.55	97	69	100	95	.011	.4	.10	88	87	102	95	.020	0	-----

[1] Acid calculated as percent SO_3.

[2] Average of machine and cross directions.

Figure 1 shows the relation between the percentage retention of folding endurance after 4 years normal aging and the percentage retention of folding endurance after heating at 100° C. for 72 hours. Although some of the points, particularly in the range of higher stability, are rather widely scattered it is evident that in general the folding endurance of those papers least stable under the heat test decreased at a faster rate during the 4 years of normal aging than that of the papers which were more stable toward heat. Similarly, the papers most resistant toward heat showed the least change in folding endurance under normal aging.

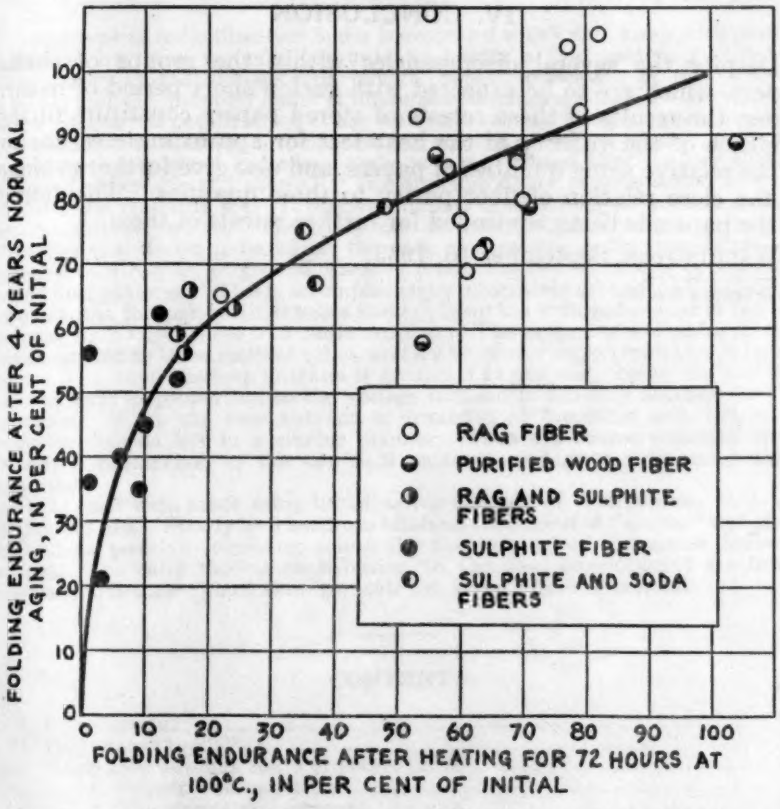

FIGURE 1.—*Comparison of retention of folding endurance after normal and accelerated aging.*

In general, the papers with the highest chemical purity were the most resistant to deterioration either by heat or normal aging, while those with the least desirable initial properties underwent more rapid deterioration. It will be noted that the most significant relation of the initial properties of these papers to their weakening during storage, and likewise under the heat test, was the purity of the fibers as measured by alpha cellulose content and copper number. An exception appears in the case of the soda-sulphite book papers, which, despite comparatively low alpha cellulose contents and high copper numbers, have fold retention values which are intermediate between those of

the best and poorest papers. It should be noted, however, that these values are probably somewhat inaccurate because of the extremely low initial folding endurance values. However, it is noteworthy that the same exception occurred under the heat test. This was ascribed [8] to the several differences in the components of this type of paper and writing paper.

It seems desirable to mention that as these papers were 4 years old, they should not be regarded as necessarily representative of the average quality of such papers at present because improvement in properties that affect permanence of papers has been the general rule during this period.

IV. CONCLUSION

Despite the several discrepancies within the groups of similar papers, which are to be expected with such a short period of natural aging, the results of these retests of stored papers constitute further evidence of the validity of the heat test for approximate estimation of the relative aging qualities of papers, and also give further evidence of the close relation of fiber purity to these qualities. The storage of the papers is being continued for further retests of them.

WASHINGTON, September 16, 1933.

[8] See footnote 2, p. 727.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP621

Part of Bureau of Standards Journal of Research, Vol. 11, December 1933

A RADIO DIRECTION FINDER FOR USE ON AIRCRAFT

By Wilbur S. Hinman, Jr.

ABSTRACT

A new type of radio direction finder is described which does away with phasing difficulties by using a single loop antenna having a field pattern modified by dissymmetry in the loop-antenna circuit. Visual indication of the "course" is given, and the direction finder is bilateral and unidirectional. The indication of the "course" is not distorted at any volume level, including complete overload. The characteristics of the incoming signals are not destroyed when "on-course" indications are received, but a loud audio note is produced when the loop antenna is turned either side of "course." The direction finder may be added as a unit to any radio receiving set. It operates on any received signal, with modulated or unmodulated waves. The sharpness of indication is readily controllable. This direction finder is based on the idea of reversing a dissymmetrical loop antenna with respect to ground, thereby producing two equal but opposite distorted field patterns. This is accomplished by alternately grounding the ends of a loop antenna through rectifier tubes and applying the voltage induced in the loop antenna by a radio wave to a radio receiver. The output of the radio receiver is also applied to these rectifier tubes, and a zero-center course indicator is so connected that when the loop antenna is grounded at one end, the course indicator deflects right in proportion to the voltage induced in the loop antenna for that condition. When the loop antenna is grounded at the other end, the course indicator deflects left in a similar manner. Thus the course indicator shows directly a comparison of the two field patterns, and gives zero-center course indication.

Flight tests were made using broadcasting stations of Washington, D.C., and Baltimore, Md. Steady and accurate bilateral indication of "course" was given, as well as positive localizing action (by the reversal of the course indicator action). The early models contributing to the final development are briefly discussed and their circuit arrangements are given where of interest.

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I. INTRODUCTION

The need for an accurate marking of the principal air routes of the country has been well met by the installation of radio range beacons. Their operation over a number of years shows quite definitely that they are satisfactorily devised for guiding aircraft. The limitation, however, is that they may only be used on the particular air routes for which they were installed. The itinerant pilot cannot always use them. Thus there is the need for a direction finder operating as

a radiocompass with which the pilot may be guided to a point to which radio range beacons are not available.

The following general requirements were considered essential for a satisfactory aircraft direction finder:

(1) It must give accurate bilateral indication with no mechanically moving parts. (Moving parts are cumbersome and liable to failure.)

(2) It must be capable of being added as a unit to a standard radio receiver with no adjustments other than tuning and control of volume. (Phasing of currents must be accomplished automatically.)

(3) It must give definite directive sense with no false courses. (That is, there should be one true course, with neither 90° nor 180° ambiguity.)

(4) It should operate both on modulated and unmodulated radio waves and should not destroy the characteristics of the received signal.

II. PRELIMINARY MODELS

The well-known Robinson direction finder with two crossed-loop antennas was used as a basis for development. The first model consisted of the mechanical reversal of one loop antenna with respect to the other by means of a rotating coil in a coupling system. The output of the radio receiver was applied to a zero-center course-indicating meter through a reversing switch operated in synchronism with the rotating coil. Indication right and left of "course" was obtained, but the 90° courses introduced by the two crossed-loop antennas and the mechanically moving parts made this model far from promising as a direction finder.

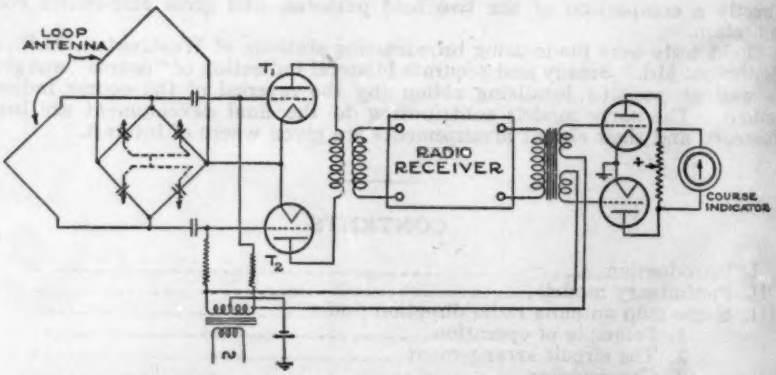

FIGURE 1.—*Double-loop-antenna direction finder with Bellini-Tosi bridge condenser tuning arrangement and electrical switching.*

Electrical switching was then tested, using the 2 crossed-loop antennas with 2 input and 2 output tubes which were alternately operated and cut off in pairs by an alternating voltage applied to their grids. The loop antennas were tuned by a special bridge condenser arrangement developed by Bellini-Tosi, which seemed especially adaptable to this direction finder by reason of the combination of the currents in the condensers. The circuit arrangement is shown in figure 1. This direction finder also gave indication right and left of "course", but it had 90° courses. It had the further disadvantage that extreme

care was necessary in the adjustment and matching of the input and output tubes.

A model was then constructed, using the idea of alternately connecting and disconnecting one loop antenna, and utilizing a special output switching arrangement. The operation is best explained by reference to the circuit arrangement shown in figure 2. The loop

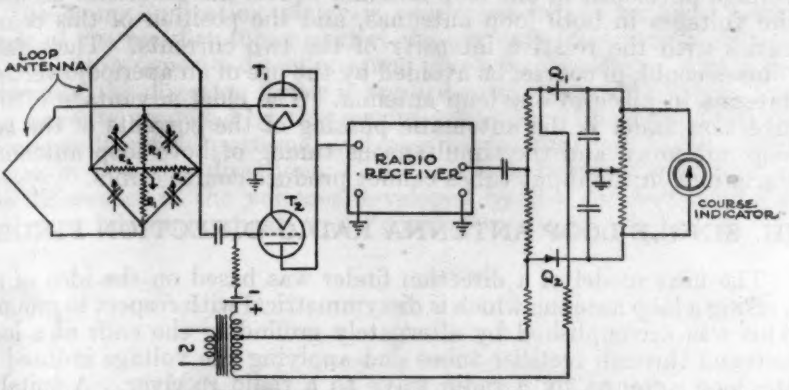

FIGURE 2.—*Double-loop-antenna direction finder with modified Bellini-Tosi bridge condenser tuning arrangement.*

antennas and bridge condenser arrangement is similar to that previously described. The currents of the two loop antennas are separated by the four resistors R_1R_1, R_2R_2. R_1R_1 carry the current of one loop antenna and are applied to T_1, and R_2R_2 carry the current of the other loop antenna and are applied to T_2. Tube T_2 is alternately operated and cut off by means of an alternating voltage applied to its grid, so that the voltage applied to the radio receiver is alternately the voltage of one loop antenna, and the sum or difference of the voltages of both loop antennas. The output device consists of two copper-oxide rectifiers Q_1 and Q_2 connected to a zero-center course indicator so that they pass current through the course indicator in opposite directions. Then, if equal alternating voltages opposite in phase are applied to the rectifiers, equal and opposite currents will flow through the course indicator. This alternating voltage is supplied from the source which operates T_2, so that T_2 operates with one rectifier and is cut off with the other rectifier. The output voltage of the radio receiver is superimposed on the alternating voltages applied to the rectifiers. Then when a signal is received Q_1 passes current due to one loop antenna (the other loop antenna being cut off by T_2), and Q_2 passes current due to both loop antennas (T_2 being in an operating condition). If the loop antenna whose voltage is applied to T_2 is at minimum with respect to an incoming radio wave, the loop antenna applied to T_1 gives the whole signal applied to Q_1 and Q_2, and the course indicator is at zero. If, however, the loop antenna supplying T_2 is not at minimum, then Q_1 passes current due to the voltage developed in one loop antenna, and Q_2 passes current due to the voltage developed in both loop antennas. The voltage developed in both loop antennas is either greater or less than that due to one loop antenna, depending on the phase relations of the currents. This gives right and left indications of "course", since for

one side of "course" the current due to the voltages of the loop antennas will aid and for the other side of "course" they will oppose each other.

While this direction finder gave more promise than any of the other models, the two crossed-loop antennas were cumbersome and the tuning system was bulky. Two false courses are found where the voltage developed in one loop antenna equals the difference between the voltages in both loop antennas, and the position of this course varies with the relative intensity of the two currents. These false courses could, of course, be avoided by the use of an aperiodic vertical antenna in place of one loop antenna. The chief advantage of this direction finder is the automatic phasing of the currents of the two loop antennas, and the simultaneous tuning of both loop antennas. Variations in the input tubes cannot produce course errors.

III. SINGLE LOOP ANTENNA RADIO DIRECTION FINDER

The next model of a direction finder was based on the idea of reversing a loop antenna which is dissymmetrical with respect to ground. This was accomplished by alternately grounding the ends of a loop antenna through rectifier tubes and applying the voltage induced in the loop antenna by a radio wave to a radio receiver. A suitable output system synchronized with the input tubes, and applied to a zero-center course indicator was connected to the output of the radio receiver. The course indicator was made to deflect to the right when the loop antenna was grounded at one end, and to the left when the loop antenna was grounded at the other end in proportion to the signal developed for the two conditions. It was immediately evident that this direction finder was worth further development.

1. PRINCIPLE OF OPERATION

For a number of years it has been common practice to introduce into a balanced loop antenna sufficient voltage from a vertical antenna to change the normal figure-of-eight field pattern of the loop antenna into a cardioid. Methods for accomplishing this are well known, the requirements being that the vertical antenna current be 90° out of phase with the loop antenna currents, or in phase with their resultant. Since a loop antenna which is not symmetrical with respect to ground tends to act partially as a vertical antenna, this cardioid type of field pattern can be approached without the use of a vertical antenna. Careful adjustment of the tuning of the loop antenna is necessary to adjust accurately the phases of the currents due to the vertical effect and the loop antenna effect if perfectly phased patterns are desired, but modified patterns of various types are very readily secured. Some of these modified patterns are shown in figure 3, the blunted minima being due to a phase angle between the vertical effect and loop antenna effect. If any one of these field patterns be rapidly reversed so that two equivalent field patterns are produced alternately (figure 3 (d)), and if a zero-center course-indicating meter be made to deflect to the right in proportion to one field pattern, and to the left in proportion to the other field pattern, bilateral indication of direction results. It is obvious that the two positions giving zero or "on course" indications on the meter are at right angles to the plane of the loop antenna and 180° apart, since each field pattern is symmetrical about the line representing the loop antenna.

The field pattern of the loop antenna is both modified and reversed by grounding the ends of the loop antenna through two rectifier tubes to which an alternating voltage is applied so that they pass current alternately. When one rectifier passes current its resistance is low, and the loop antenna is effectively grounded at that end. The loop antenna is tuned, and the antenna effect made partially aperiodic by the resistance of the rectifiers.

The course-indicating meter is connected in the cathode return leads of the rectifier tubes so that the currents of the rectifiers pass through it in opposite directions, and give a zero reading. The audio output of the direction finder is applied to the rectifier tubes so that the currents produced by this output voltage are proportional to the corresponding field patterns, and pass through the course indicating meter in opposite directions. The course indicator then indicates the differences in the voltages developed by the two field patterns, and gives bilateral indication of "course."

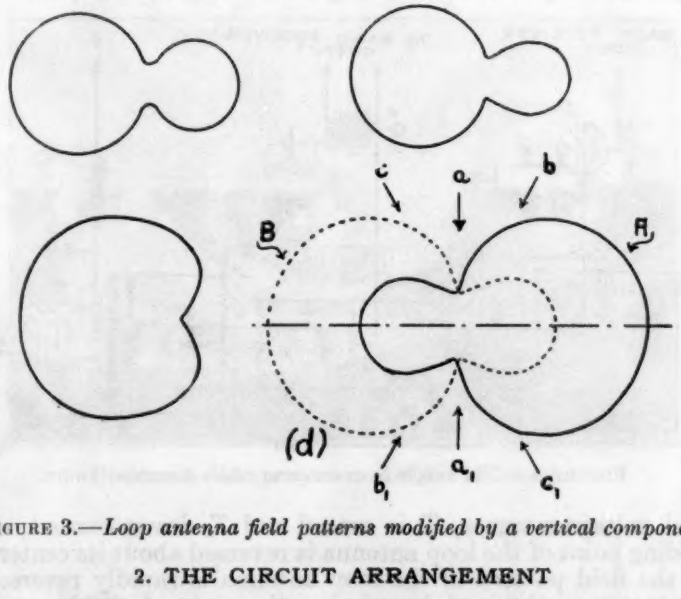

FIGURE 3.—*Loop antenna field patterns modified by a vertical component.*

2. THE CIRCUIT ARRANGEMENT

The circuit arrangement is given in figure 4. Condenser C_1 tunes loop antenna L_1 and any voltage developed in the loop antenna by an incoming radio wave is applied to the first radio-frequency amplifier between the center point of the loop antenna and ground. The loop antenna is connected at each end to rectifier tubes T_1 and T_2 through equal condensers C_2 and C_3. An alternating voltage of a frequency readily passed by the audio amplifier of the radio receiver is applied in opposite phase through radio-frequency inductors L_2 and L_3 to the plates of the rectifier tubes. The cathodes of the rectifier tubes are connected one to each end of resistor R_1, the adjustable center tap of which passes through the audio output transformer of the radio receiver to ground. The zero-center course-indicating meter M is connected across this resistor. Condenser C_5 is a high-capacity low-voltage electrolytic condenser which damps course

indicator M. An audio oscillator consisting of oscillation transformer O and vacuum tube T_4 with tuning condenser C_4 supplies voltage to rectifiers T_1 and T_2 across voltage divider R_2 R_3. R_2 and R_3 are equal resistors accurately matched to about one half of 1 percent to insure equal voltages of opposite phase for rectifiers T_1 and T_2. R_4 may be added to the circuit to reduce the effect of any changes in the resistance of the rectifier tubes. Greater sensitivity will result if it is omitted. R_5 and R_6 are biasing resistors, and R_7 provides a grid return for first radio-frequency amplifier T_3. Output transformer O_2 applies the output of the radio receiver to rectifier tubes T_1 and T_2 and allows them to operate as the output switching device in addition to their function of alternately grounding the ends of the loop antenna.

From figure 4, when a positive voltage is applied to the plate of T_1 by the audio oscillator, a negative voltage is applied to the plate of T_2. Then T_1 draws current and has low resistance to ground, and T_2 is cut off with high resistance to ground. When the phase of the

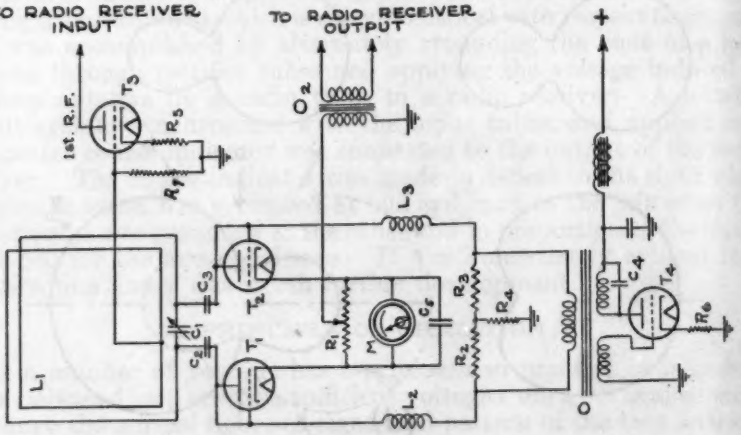

FIGURE 4.—*The single loop antenna radio direction finder.*

applied voltage reverses, T_1 is cut off and T_2 draws current, and the grounding point of the loop antenna is reversed about its center point. Thus the field pattern of the loop antenna is rapidly reversed, and dissymmetry is obtained by placing the ends of the loop antenna alternately at ground.

The currents of T_1 and T_2 produced by the voltage of the audio oscillator pass through course indicator M in opposite directions. Since the voltage of the audio oscillator is applied equally to these rectifiers, the currents are equal and the course indicator reads zero. Remembering that when T_1 passes current one loop antenna field pattern is produced and current passes through the course indicator in one direction, and when T_2 passes current another field pattern is produced and current passes through the course indicator in the other direction, consider the effect of an incoming radio wave. When the loop antenna is grounded at one end, the signal at the output of the radio receiver is proportional to the field pattern for that condition and the current through the course indicator is proportional to the

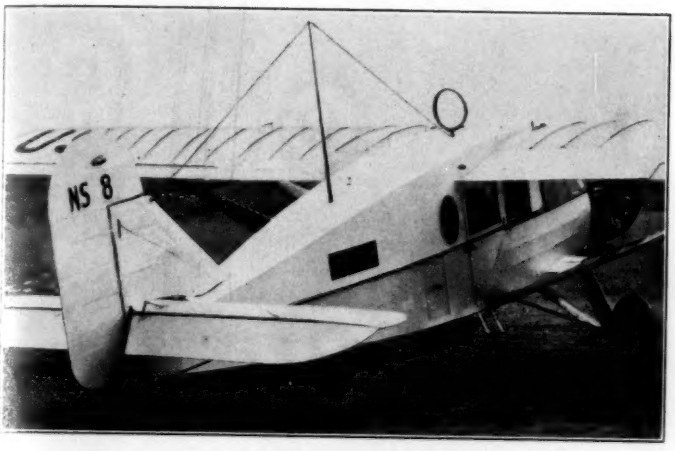

FIGURE 5.—*Loop antenna installed on airplane.*

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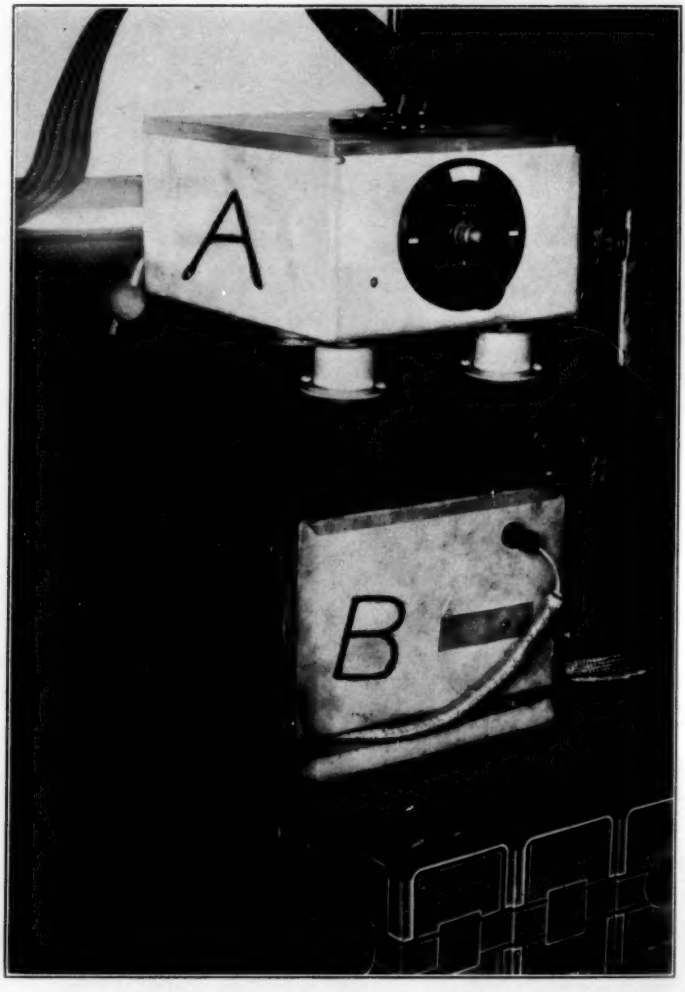

FIGURE 6.—*Single-loop antenna direction finder unit A and radio receiver B installed for test in airplane.*

voltage of the audio oscillator and the output voltage. When the loop antenna is grounded at the other end similar conditions hold, but there is a reversal of current in the course indicator. Since the currents through the course indicator due to the audio oscillator are equal and opposite, currents deflecting the course indicator right or left are directly proportional to the difference between the output voltages due to each field pattern.

There are two positions of the loop antenna with respect to an incoming radio wave which gives "on-course" indications. These two positions are at right angles to the plane of the loop antenna and 180° apart. It can be seen from figure 3 (d) that the action of the course indicator for one course is the reverse of its action for the other course, giving automatic directive sense. Let A and B be the field patterns developed by the loop antenna, the course indicator deflecting to the right when A is produced, and to the left when B is produced. When a radio wave is received from direction a the field patterns are equal and "on course" reading results. If the radio wave comes from direction b, A is much larger than B, and the course indicator reads to the right of "on course." The loop antenna must then be rotated to the right for an "on course" indication. Similarly, a signal from direction a_1 gives an "on course" indication, but a signal from b_1 produces a reading to the left of "on course", which is the reverse of the indication for a signal from direction b. By following the rule that when heading toward the source of the signal the indicator deflects in the direction the loop antenna is "off course", directive "sense" is assured.

3. CONSTRUCTION

In the construction of the direction finder, care must be taken that the loop antenna is symmetrical about its center point with respect to ground. There should be no displacement current or secondary loop antenna effect. This is avoided by using a narrow type of winding in the loop antenna. The plate circuits of the two rectifiers must also be balanced for equal inductance and capacity. A slight distortion of "course" results when these circuits are not balanced. The loop antenna may be mounted at a distance from the radio receiver and the direction-finder unit, but the leads connecting these units should be fixed in position by a web belt or some similar means, and the capacity to ground should be low. Resistors R_2 and R_3 must be matched to about one half of 1 percent. Type 237 tubes are used as rectifiers, the grids and plates being connected together. Variation in the resistance of these tubes has little effect on the field pattern produced. In the output circuit, since it depends on the balancing of currents, the rectifiers should be fairly well matched. R_1 serves to complete the matching of the rectifiers. It is adjusted for zero reading of the course indicator when no signal is being received.

4. TESTS

The direction finder has been installed and tested on an airplane at College Park. A photograph showing the installation of the loop antenna on the airplane is given in figure 5, and the direction-finder unit with the radio receiver is shown in figure 6. The direction-finder unit A with the belt connection to the loop antenna is at the upper

left of the installation, and the control unit for the radio receiver is mounted beside it. The radio receiver *B* is directly below the direction-finder unit. Figure 7 shows the course indicator. Test flights were made in the vicinity of Washington and Baltimore, using the broadcasting stations of those two cities. In these tests the direction finder was used as a homing device. Its operation was entirely satisfactory, indications right and left of "course" being very steady and definite. On passing over the stations toward which the flights were made, positive localizing action was given by the reversal of the action of the course indicator. Although the locations of the various stations

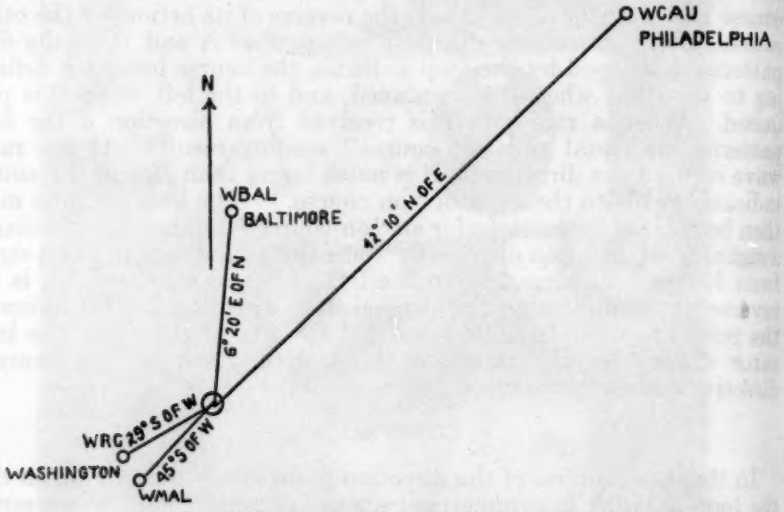

FIGURE 8.—*Typical direction-finder bearings taken at College Park.*

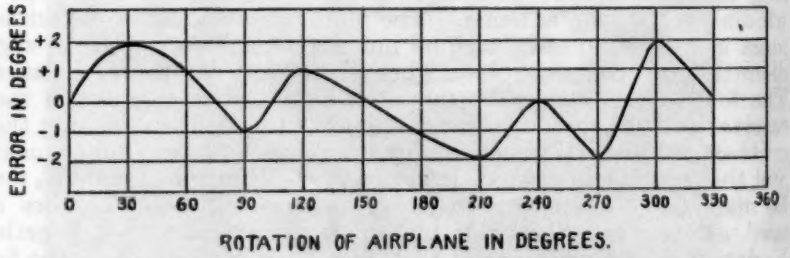

FIGURE 9.—*Calibration graph for errors introduced by airplane structure.*

were unknown to the pilot in each case, he immediately located the station to within a half mile radius from an altitude of about 3,000 feet.

Figure 8 shows triangulation data taken on the ground at College Park, Md. A magnetic compass was used as a basis for the measurements. Figure 9 gives the error in indication for the loop antenna installation on the airplane.

The accuracy of the direction finder is of the order of 1°. The sensitivity of the indications varies with volume, and it can be very easily increased or decreased by changing the circuit constants. Full-scale deflection of the course indicator for 10° variation from "course"

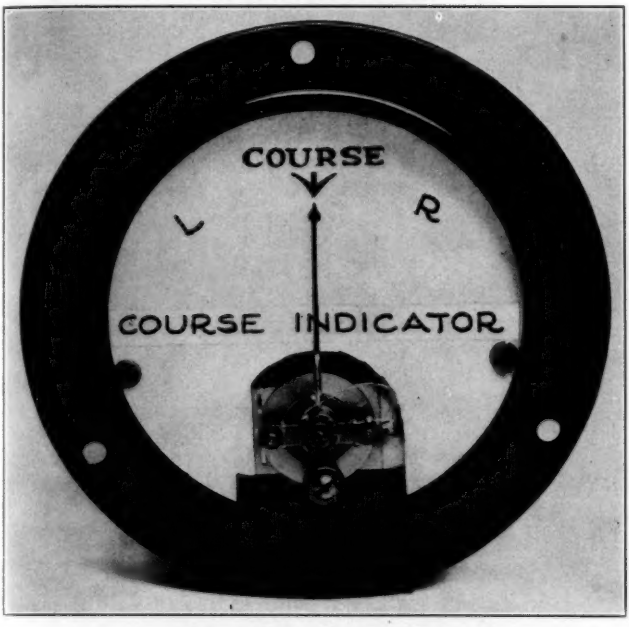

FIGURE 7.—*Course indicator.*

is readily secured. No distortion of "course" could be noticed at any volume level, including complete overloading of the radio receiver. An interesting feature of the direction finder is its action under conditions of bad static or ignition interference. When "on-course" signals are received there is little effect, and when "off-course" signals are received any change in indication tends toward an "on-course" indication. No violent kicking of the course indicator occurs.

Signals are intelligible while the direction finder is operating. When "on course", only a constant tone of low intensity being present in the radio receiver. When "off-course" indications are received, this tone increases in intensity, tending to destroy the characteristics of the incoming signal. Aural check on the course indication is thus given.

The direction finder operates equally well on modulated or unmodulated waves. When the radio wave is intermittent, the direction finder operates only when the radio wave is received. In this case indications right and left of "course" are given by a kicking of the course indicator right and left from zero. The "on-course" indication is constant.

There is practically no tuning error if the loop antenna is resonated at, or above, the frequency of the station on which the bearing is taken. If the loop antenna is resonated below this frequency, the field patterns may be badly distorted by the reversal of phase of the loop-antenna current, thus producing course errors. The loop antenna, then, may either be tuned or untuned, providing that its resonant frequency is never lower than that of the station on which the bearing is being taken.

IV. ACKNOWLEDGMENT

Acknowledgment is made to H. Diamond for basic contributions in some of the earlier models, and for many helpful suggestions in connection with the final development, and to L. L. Hughes for skill in construction of the various models. G. H. Lester gave valuable assistance in the construction and testing of the final model.

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THE PHOTOGRAPHIC EMULSION: SENSITIZATION BY SODIUM SULPHITE

By Burt H. Carroll and Donald Hubbard

ABSTRACT

Sodium sulphite, in quantities sufficient to reduce a few tenths percent of the silver bromide of a photographic emulsion, may act as a powerful sensitizer only slightly inferior to the natural sensitizers in gelatin. It acts as such only after digestion with the emulsion, insuring that it has reacted with the silver bromide. The sensitivity nuclei thus formed are of metallic silver, in amounts similar to the silver sulphide nuclei of normal emulsions. The rate of change of sensitivity increases with increasing alkalinity and decreases with increasing bromide-ion concentration. Sulphite may be added to the emulsion before washing, sensitizing only on digestion after washing. There was no indication of panchromatic sensitization (Capstaff effect).

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I. INTRODUCTION

It has long been known that if pure silver bromide is precipitated from water solutions and subsequently suspended in gelatin, the resulting photographic emulsion is very insensitive. While there are difficulties connected with the emulsification under these conditions, it suggested that the grains of an emulsion may not be pure silver bromide (or bromide-iodide). Further evidence was supplied by Lüppo-Cramer's discovery[1] (1), later extended by Clark, (2), (3), (4), and others, that the sensitivity of ripened emulsions was greatly reduced by treatment with oxidizing agents, such as chromic acid, which do not attack silver bromide. Statistical studies of the sensitivity of individual grains and of the distribution of the development

[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the paper.

centers on them (5) indicated that it is highly probable that the unexposed grains of an emulsion contain nuclei which are different from the rest of the grain, and a most important factor in sensitivity. Finally, Sheppard and his coworkers (6), (7) demonstrated the existence of materials which act as powerful sensitizers for emulsions when used under conditions which insure the formation of a trace of silver sulphide by reaction between silver bromide and the sensitizer.

The hypothesis naturally suggested by the desensitizing action of oxidizing agents was that traces of silver bromide had been reduced during the ripening process to silver. It has never been definitely proved or disproved that the nuclei of ripened emulsions contain metallic silver. Clark (8) attempted to distinguish between silver and silver sulphide by means of oxidizing agents of varying potential, without conclusive results. Weigert and Lühr (9) believed that they had proved by treatment with persulphate that the "Ursilber" (silver not combined with halogen) could not be silver sulphide, but this has since been found (10), (11) to be incorrect. On the other hand, Carroll and Hubbard (12) demonstrated that colloidal silver may, under special conditions, sensitize an emulsion, apparently by functioning as nuclei after adsorption to the grains. In this paper it is shown that sodium sulphite may have photographic-sensitizing action approaching that of allyl thiocarbamide, when it is added to emulsions under such conditions that it must reduce traces of the silver bromide to metal. The hypothesis that metallic silver may act as sensitivity nuclei, therefore, appears to be proved. Reduction of the silver bromide before exposure normally causes fog, exactly analogous to the fog produced by the formation of silver sulphide from inorganic sulphides. This turns out to be fresh proof of the fact that has become increasingly evident (14) lately, that the quantity of nonhalide silver in an emulsion is much less important than what we may call its quality for want of more definite knowledge. Sheppard (6), (15) has observed that all the sulphur, selenium, and tellurium sensitizing compounds specified by him form complexes with silver halides, and that no sensitization is produced by equivalent amounts of inorganic sulphides. Sodium sulphite is closely analogous. Difficultly soluble silver salts may be dissolved in sulphite solutions by formation of a complex ion, probably $Ag(SO_3)_2^-$, similar to that formed by thiosulphate or thiocarbamide. The mechanism of reduction in one case and sulphide formation in the other is probably the same. This will be discussed in a separate paper on the kinetics of these reactions.

One hypothesis which cannot be excluded on the present evidence is that the presence of both silver and silver sulphide is essential to sensitization. Sheppard and Punnett (16) have patented the use of reducing agents such as sodium "hydrosulphite" (but not sulphite) in combination with sensitizers giving silver sulphide, and Trivelli has elaborated a theory (17) of sensitivity and the latent image based on a compound nucleus. Under the conditions of the experiments to be described in this paper, silver should have been formed in proportions greater than silver sulphide, but no gelatin emulsions can be proved to be free from the latter. Some light might be thrown on this point by testing the sensitizing action of sulphite on emulsions made up in gum arabic known to be free from labile sulphur.

The addition of sulphite to photographic emulsions is by no means new; the novelty of our results depends on the conditions of its use.

The earliest references (13) are to the combined use of sulphite and ammonia, which caused so much reduction that a mirror was deposited on the walls of the vessel, with consequent fog. Valenta (18) digested Lippmann emulsions with 1g Na_2SO_3 to 300 g emulsion at 38°. The sulphite retarded growth of grain; plates ripened up to 30 minutes could be used for the Lippmann process, while without it, the grain grew enough to give duller colors. Emulsions which were 4° Warneke after 5 minutes digestion with the sulphite were 18° after 1 hour digestion. Lüppo-Cramer (19) reports that bromine absorbents such as sulphite may increase the sensitivity of Lippmann emulsions, but the evidence in the case of Valenta's work is that the sensitization was the result of reaction of the sulphite and silver bromide, since prolonged digestion was necessary for the full effect. This feature of Valenta's work has escaped notice, although the statement about the grain size has not; in the one recent reference (20) to the use of sulphite in an emulsion formula, Valenta's experiments are said to have inspired the idea of adding sulphite to produce fine grain and high contrast.

Collodial silver in emulsions has frequently been observed to cause spectral sensitization; this effect, which has recently been reviewed by Sheppard (22), is well established, while general sensitization by silver has remained a matter of conjecture. Silver sulphide is capable of producing both effects—general sensitization when materials such as allyl thiocarbamide are added to the emulsion before digestion, and spectral sensitization when plates are bathed in the same materials, or when silver bromide and colloidal silver sulphide are precipitated together to form the analogue of the photobromide. In this case, Sheppard has concluded that the spectral sensitization is caused by larger numbers of very fine silver-sulphide particles, while the general sensitization is caused by fewer and coarser nuclei. Similar results are to be expected with silver. The analogy is apparently complete, since we have obtained general sensitization by adding sulphite to the emulsion before digestion, while Capstaff and Bullock (21) found that some emulsions (Eastman Portrait film) acquired panchromatic sensitivity by bathing in solutions of sodium bisulphite and washing in dilute alkali. The alkali was necessary to the sensitization, while soluble bromide prevented it. It was accompanied by visible discoloration of the emulsion. All this evidence indicates that the silver halide of the emulsion was reduced by the sulphite, so that the sensitization may be attributed to colloidal silver.

Investigation of photographic emulsions at this bureau has been suspended for lack of funds. The experimental data here presented are admittedly incomplete in some respects, which we have attempted to indicate, but the results seem to be quite adequate to justify publication.

II. EXPERIMENTAL

1. THE REACTION BETWEEN SODIUM SULPHITE AND EXCESS SILVER BROMIDE

Data on the kinetics of the reduction of silver bromide by dilute solutions of sodium sulphite will be given in a separate communication. The reaction may be written $2\ AgBr + Na_2SO_3 + H_2O = 2\ Ag + 2\ NaBr + H_2SO_4$. It is retarded by the products, hydrogen and bromide ions. Under the conditions of sensitization in the emulsion, which involve reduction of not over 0.01 percent of the silver

bromide, the change in concentration of these ions produced by the reaction itself is negligible.

While nothing was found in the literature to indicate that there might be side reactions, the known tendency of solutions of sulphur dioxide to form thiosulphuric and polythionic acids made it essential to test the products of the reaction for silver sulphide. Silver bromide or chloride was boiled with sodium sulphite solution, the former being in excess. The solid reaction products were oxidized with concentrated nitric acid. No sulphate was found after this treatment, although it would have been determined if as little as 0.1 percent of the silver reacting had gone to sulphide.

As the tendency for rearrangement of sulphite solutions is greatest at the boiling point, these experiments should have been an adequate test and we may say that the sensitizing action of sodium sulphite on emulsions cannot be explained by formation of silver sulphide.

The sodium sulphite used in the experiments was a c.p. product of unusually high grade, assaying 99 percent Na_2SO_3 by iodine titration. It was tested for the presence of thiosulphates or polythionates by the sensitive azide method of Feigl (24) with completely negative results. Stock solutions, about tenth normal, were kept under hydrogen, maintaining their titer unchanged for over a week.

The hypothesis that the sulphite may act simply as a bromine absorbent is satisfactorily eliminated by the complete absence of any immediate effect on sensitivity. In two cases where marked sensitizing action was developed on subsequent digestion with the sulphite (emulsions 4-124 and 125, fig. 4), the emulsion directly after its addition was, within the limits of error, no different from the controls. Using the speed number $10/E_m$ (for 6-minute development) in one case the control was 11, the batch with sulphite 10; in the other case the figures were 10 and 10.5. The sulphite-sensitized portions developed speeds of 1,400 and 300, on the same basis, on subsequent digestion.

2. PREPARATION OF EXPERIMENTAL EMULSIONS

The general methods of making experimental emulsions in this laboratory have been described in other papers. The formulas used in the experiments where sulphite was added after washing will be given in full at this point; some of the experiments with sulphite in the original mix of the emulsion will be described in a later section. Practically all the emulsions were of the neutral type. The sensitizing effect of sulphite was first tested by adding sodium sulphite or sulphur dioxide solutions to washed emulsions which had been made by the ammonia process, but no experiments have been made by adding sulphite to the original solutions of an ammonia-process emulsion. It is probable that sensitization could be produced in this way, but the sulphite would be rapidly oxidized by the air under these conditions and difficulty in reproducing results is to be anticipated.

All the emulsions were washed by the conventional method of shredding the set jelly and extracting with cold water. Except for a few otherwise noted, they were washed in changes of distilled water plus 1¼ g $MgSO_4 \cdot 7H_2O$ per liter, using the apparatus described in a recent note (25). This has been improved by the addition of a

stirring device. A cam rotating about three times a minute, slowly lifts the nickel-gauze basket containing the emulsion 4 cm, then drops it suddenly through the water. This has more than doubled the rate of washing; there is very little loss of emulsion since the noodles are not scraped against the wire gauze as by rotary stirring.

The formula most used has already been described under the designation of "C" in a previous paper (27); it will be referred to as C-1 in this case. The solutions are:

NH_4Br (0.429 g equivalent)	42.0 g	$AgNO_3$ (0.353 g equivalent)	60.0 g
KI (0.0139 g equivalent)	2.30 g	Water	450 ml
Gelatin	20 g		
Water	350 ml		

With both solutions at 65° C., the silver was run into the bromide solution in a fine stream with rapid mechanical stirring in 25 ± 2 minutes. Directly after this, 80 g of gelatin, previously swelled in cold water and drained, was added in small amounts; it was completely dissolved in 8 to 10 minutes and the emulsion was then chilled rapidly. It was usually allowed to set over night before shredding and washing; even with active gelatin the ripening during this period is negligible. After washing, it was digested, this time at 55° C., and known bromide- and hydrogen-ion concentrations. At appropriate intervals, samples were taken out and test plates coated. Results with this formula, using deactivated gelatin and sensitization by allyl thiocarbamide added before digestion are recorded in figure 3.

A modification of the formula, which will be known as C-2, may be used for higher speeds with somewhat lower contrast.

NH_4Br (0.565 g equivalent)	55.3 g	$AgNO_3$ (0.47 g equivalent)	80.0 g
KI (0.0234 g equivalent)	3.90 g	Water	600 ml
Gelatin	21 g		
Water	350 ml		

In this case, the AgI has been raised to 5 mol percent. The concentration of the bromide solution has been raised in order to maintain the solubility of the silver halide and thus the grain size. The solutions were mixed in 33 ± 2 minutes at 65° C. After mixing, 110 g swelled gelatin was added in about 10 minutes and the emulsion chilled. Washing and digestion were carried out as for C-1.

One of the problems connected with any experiments on sensitizing compounds lies in the control emulsions. It is, as far as we know, impossible to prepare a gelatin which is truly inert photographically. Digestion after washing, at relatively low bromide-ion concentrations and pH of 6 or over, is apparently the most severe test of inertness; special gelatins stated by their manufacturer to be inert under other conditions were found to be quite active during digestion. As stated in a previous paper (12) some samples of gelatin can be very considerably deactivated by digestion with ammonia followed by thorough washing. About half the emulsions were made with a deactivated gelatin of this type which will be designated as "gelatin 1." "Gelatin 2", of about the same activity as the previous lot, was prepared from a batch of Nelson no. 2 gelatin. This was extracted first with dilute sulphuric acid, the pH of the gelatin being lowered to about 3, then washed thoroughly in tap water, coming out approximately isoelectric. It was then extracted with dilute ammonia, and washed again; the final pH was about 7. The control emulsions with these gelatins are recorded in figures 3 and 8.

3. SENSITOMETRY

The experimental plates were tested by the standard methods of this bureau: Nonintermittent time-scale exposure at an intensity of 1 meter candle of sunlight quality, brush development in pyrogallol without bromide for 3, 6, and 12 minutes at 20° C. and measurement of densities in diffuse illumination. The sector wheel used in this laboratory is of the conventional Hurter and Driffield pattern with 9 steps in ratio of 2. For all tests reported in this paper, 2 exposures were made, differing by 0.09 to 0.15 on the log E scale, so that 18 points on the characteristic curve were obtained. Use of the pyrogallol developer has been continued for comparison with earlier work. Some of the emulsions were also developed with the standard p-aminophenol formula (28) and with the metol-hydroquinone formula tentatively recommended by Davis and Neeland (29). As far as could be determined, the results are parallel with any of these developers; there is

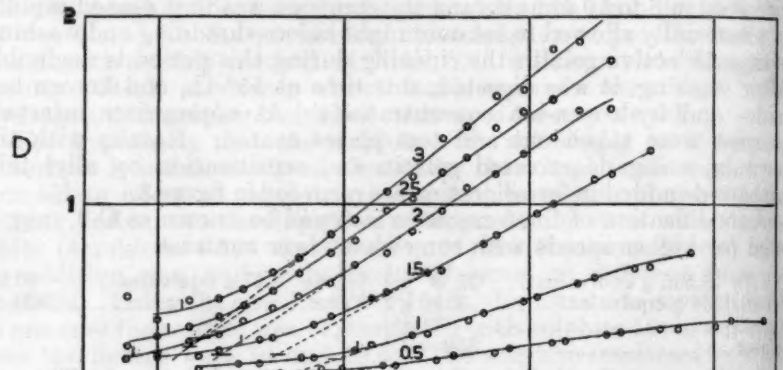

FIGURE 1.—*Characteristic curves for 6-minute development of emulsion 4-178 after digestion in vacuum with sodium sulphite for ½, 1, 1½, 2, 2½, and 3 hours.*

C-2 emulsion formula made with gelatin 2, digested with 1.7 mg sodium sulphite per g silver bromide at 55°, pH 7.4 [Br^-] 5×10^{-4}. This amount of sulphite corresponds to a ratio of 6×10^{-3} in terms of chemical equivalents.

no indication that the sulphite sensitization introduces any peculiarities of development.

Representation of the results without resorting to an undesirable use of tables gives the usual difficulties. The change in sensitivity on digestion with sulphite is such that the shape of the characteristic curve is altered, with changes in speed, contrast, and relative length of "toe", very much like the corresponding results on digestion of a normal emulsion (27). The type of change is illustrated by the characteristic curves plotted in figure 1 and the corresponding numerical values in table 1. After comparing different methods of plotting the results, it was decided to use the value of $10/E_m$ (where E_m is the exposure corresponding to the "minimum useful gradient" of 0.2) for 6-minute development as the best approximation to a single index of sensitivity. The characteristic curves of either type of emulsion have satisfactory straight-line portions and it would be possible in

most cases to give the data in the form of $10/i$ at a constant γ. However, this would exclude a number of batches in the early stages of digestion, and would give little improvement in the accuracy of representation of the individual points. Our conclusions are, of course, in all cases based on comparison of the complete characteristic curves, and not merely on the numbers plotted in our figures.

TABLE 1.—*Sensitometric data for emulsion 4-178 at varying time of digestion with sodium sulphite; cf. figure 1, characteristic curves at 6-minute development, and figure 6, speed ($10/E_m$) vs. digestion time*

Digestion time, hours	Speed						γ			Fog		
	$10/E_m$			$10/i$								
	3	6	12	3	6	12	3	6	12	3	6	12
0.5	------	------	25	87	100	72	0.12	0.15	0.27	0.00	0.02	0.08
1.0	87	87	150	170	220	140	.24	.30	.65	.02	.03	.11
1.5	175	400	590	310	345	325	.37	.53	.77	.03	.05	.13
2.0	320	1,300	1,250	470	590	525	.44	.64	.95	.05	.07	.13
2.5	600	1,300	1,380	740	790	760	.42	.67	1.00	.08	.13	.18
3.0	460	1,000	1,400	560	580	490	.50	.82	1.26	.12	.21	.29

4. SPECTRAL SENSITIVITY OF SULPHITE-SENSITIZED EMULSIONS

No change in relative spectral sensitivity on sensitizing with sulphite has been evident in any case, but in view of the nature of the sensitizing produced by bathing in bisulphite solutions (the Capstaff effect) it was advisable to make a careful determination of this feature of the process. The effect to be anticipated is an extension of the natural sensitivity to the longer wave lengths. In order to detect this, exposures were made with a glass prism spectograph using a gas-filled incandescent lamp as light source. The instrument which was used is quite free from stray light, but in order to reduce both this difficulty and the spreading of the image by scattering of light within the emulsion itself, a Wratten "minus blue" filter was placed over the slit.[2] The plates were brush developed to insure uniformity. The plates which were compared were taken from two emulsions made by the C-2 formula under conditions which were identical within the limits of control. Having 5 percent AgI, the sensitivity extended into the longer wave lengths relatively far for emulsions containing no dye (30). Figure 2 gives curves derived from exposures of a control (unsensitized) plate and two plates sensitized with sulphite and allyl thiocarbamide, respectively. All three were developed to a γ of 0.50. Similar results were obtained in other experiments.

It is evident that, by sufficiently accurate choice of exposure, it would be possible to have close coincidence of the density-wave length curves for the batches sensitized with sulphite and thiocarbamide, but that the control emulsion shows a distinctly more abrupt decrease of density with increasing wave length. This indicates that either type of sensitivity nucleus causes a very slight extension of spectral sensitivity. Marked panchromatic sensitization such as the Capstaff effect is obviously not characteristic of sensitization by sulphite under all conditions. As all our experimental emul-

[2] This particular filter had a transmission of 12.5 percent at 5,000 A and 1.5 percent at 4,900.

sions have been given a preliminary test exposure behind an Eder-Hecht wedge with its filter strips, any marked spectral sensitization would have been detected; none occurred.

Limited data are available on another question involving spectral sensitivity—the interrelation of sensitization by sulphite and by dyes. Sulphite, when added to the emulsion just before coating, may (31) have an appreciable hypersensitizing effect on the dye, the sensitivity to the longer wave lengths being selectively increased without a corresponding increase in the sensitivity to the blue. This is, however, distinct from the case of an emulsion which has been digested with sulphite so as to produce an increase in sensitivity independent of the action of dyes, then made color sensitive by further treatment with a dye. In such cases, the relative spectral sensitivity conferred by the dye appeared to be normal. In the most complete test of this feature of sulphite sensitization, sulphite was added to the emulsion after washing in the ratio of 2.5 g equivalents to 1,000 of silver bromide. Samples were coated directly after this and after two periods

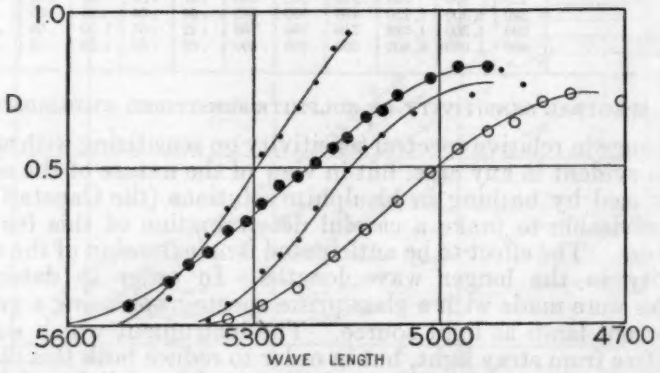

FIGURE 2.—*Densities of plates made by C-2 formula, exposed in prism spectrograph through minus blue filter, and developed to gamma of 0.5.*

● = Unsensitized control, ● = sulphite-sensitized batch, O = allyl thiocarbamide-sensitized batch. General fog density subtracted from all image densities

of digestion, each was sensitized with the same amount of pinacyanol. The resulting plates were tested for sensitivity to red and blue light by sensitometer exposures through Wratten A and C filters. Comparing the resulting speed numbers,[3] the ratio A/C was 3.1, 4.7, and 4.7 for the samples digested 0, 1, and 2 hours, respectively; the values for the undigested sample are the least reliable because of its low contrast. As the ratio remained approximately constant for a change in total sensitivity of 8 to 1, the evidence is that the formation of silver nuclei by sulphite sensitization is quite analogous to the action of allyl thiocarbamide in its effect on sensitization by dyes (6) (32).

The sulphite might have been expected to interfere with sensitization by reducing and decolorizing the dye. Apparently the dye is protected by its adsorption on the silver bromide, since sulphite in slightly larger quantities may even have an appreciable hypersensitizing action (31, table 8). The emulsion ripened with sulphite and

[3] These values are arbitrary, since they are not corrected for energy distribution of the source and transmission of the filters. Comparison was made at the constant development time of 6 minutes for each plate, since the digested and undigested samples could not be compared at the same value of gamma.

sensitized with pinacyanol, and that to which sulphite was added just before coating for the tests of hypersensitizing action, were tested again (with the Eder-Hecht wedge) after 9 months' storage. There was no evident change in relative spectral sensitivity in any case, indicating that the sulphite had not reduced the dye on storage. The white-light sensitivity had increased or decreased in some cases, depending on the degree of ripening of the emulsion.

5. THE EFFECT OF CONCENTRATION OF SENSITIZER

Other conditions being constant, the rate of after-ripening would be expected to increase continuously with the sulphite concentration, and we have found this to be the case within the limits of concentra-

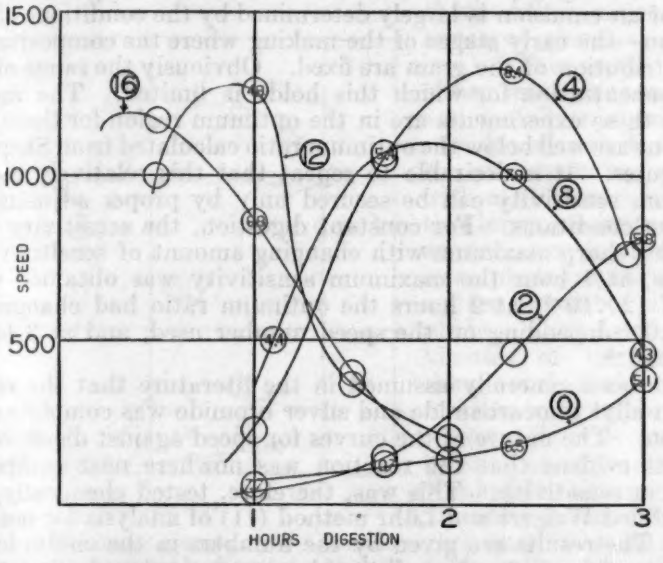

FIGURE 3.—Emulsions made by C-1 formula, gelatin 1, and sensitized by digestion with allyl thiocarbamide after washing.

The numbers of the curves indicate the ratio of allyl thiocarbamide to silver bromide in terms of chemical equivalents; for example, the figure 2 means that 2 atoms of silver per 100,000 could be converted from silver bromide to silver sulphide by the allyl thiocarbamide. Figures inside the circles representing experimental points give the nonhalide silver found in the emulsion by analysis after the digestion indicated by the location of the point; these numbers are also to be divided by 10^5 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

tion which were tested. The sensitivity, however, passes through a maximum on continued after-ripening under any conditions, and the value of this maximum is not necessarily independent of sensitizer concentration. Sheppard (33) reported that the sensitivity passed through a maximum with increasing concentration of allyl thiocarbamide, the decrease in speed being much more than would be expected simply from the increase in fog. As the conditions of his experiments were not described, we present in figure 3 the results of a similar series under the same conditions as the experiments with sulphite shown in figure 4 (C-1 emulsion formula, gelatin 1, sensitizer added after washing) for comparison with the latter. The curves of figure 3 show a progressive increase in rate of after-ripening from the control to the batch with the largest sensitizer concentration. The maxi-

mum value of each curve is not much different, on this basis of representation, for the concentrations from 4 to 16×10^{-5} g equivalent of thiocarbamide per g equivalent of AgBr; the curve for 2×10^{-5} does not reach its maximum, but the value would evidently be lower. The apparent results are in this case unfortunately affected by the method of representation; using $10/i$ at a constant value of γ for the speed number instead of $10/E_m$, the maximum speed was obtained with a ratio of 8×10^{-5} and 1 hour 40 minutes digestion; the maximum for 4×10^{-5} was decreased with respect to the others, while that for 2×10^{-5} was increased. These data indicate that the sensitivity obtainable from a given emulsion is relatively independent of the amount of sensitizer over a moderate range; this in agreement with the general experience of emulsion makers that the potential sensitivity of an emulsion is largely determined by the conditions of emulsification—the early stages of the making where the composition and size-distribution of the grain are fixed. Obviously the range of sensitizer concentration for which this holds is limited. The amounts used in these experiments are in the optimum region for these conditions, but are well below the optimum ratio calculated from Sheppard's (33) figures. It is desirable to repeat that this relatively constant maximum sensitivity can be secured only by proper adjustment of digestion conditions. For constant digestion, the sensitivity passes through a sharp maximum with changing amount of sensitizer. For example, at 1 hour the maximum sensitivity was obtained with a ratio of 12×10^{-5}; at 2 hours the optimum ratio had changed to 4 or 8×10^{-5} depending on the speed number used, and at 3 hours it was 2×10^{-5}.

It has been generally assumed in the literature that the reaction between allyl thiocarbamide and silver bromide was complete during digestion. The nature of the curves for speed against digestion time makes it evident that the reaction was nowhere near complete at maximum sensitivity. This was, therefore, tested chemically, using the modified Weigert and Lühr method (11) of analysis for nonhalide silver. The results are given by the numbers in the circles locating the points of figure 3. Not all the plates were analyzed; those chosen correspond to the optimum digestion time for a given ratio (choosing the time giving the maximum $10/i$), plus all times for the control and 8×10^{-5} ratio. Analysis for these minute traces of material is subject to considerable error in the final determination, and still more in the separation of silver halide and nonhalide silver. The reliability has been tested on synthetic mixtures, however, with satisfactory results. The data indicate that the maximum sensitivity corresponded to the formation of nonhalide silver in amounts of the order of $5-8\times10^{-5}$ g equivalent per g equivalent of silver bromide, for all amounts of thiocarbamide. It is impossible to say how much of the nonhalide silver was silver sulphide and how much was metal. The values for the controls were disconcertingly high; similar results have been obtained with other insensitive emulsions (27). It seems probable that some of the nonhalide silver comes from the traces of colloidal silver present in the best commercial silver nitrate, or is formed during mixing from contact of the silver-nitrate solution with the gelatin, or both. This does not explain the existence of larger quantities in the control than in the batches to which thiocarbamide had been added. There are no reasons for suspecting these particular data, and they are given

for what they are worth. The decrease in nonhalide silver on continued digestion has been observed before (27); oxidation of metallic silver or silver sulphide of colloidal dimensions is not improbable under the conditions of digestion, and would lead to a decrease in the silver remaining after fixation.

The data presented in figures 4, 5, and 6 show the expected increase in rate of after-ripening with increase in sulphite. For the C-1 emulsions, figure 4, the time required to reach a given sensitivity is, very roughly, inversely proportional to the sulphite-AgBr ratio. For the C-2 emulsions, figures 5 and 6, the change in rate of after-ripening is much less than the change in sulphite. It will be noted at once that the quantities of sulphite used are of the order of 20 to 50 times as great as the allyl thiocarbamide used for the same effect (both being expressed in terms of chemical equivalent). This could indicate either that the chemical reaction of silver bromide with sulphite is much slower than the corresponding reaction with allylthiocarbamide, or that larger amounts of silver are necessary to produce the same photographic effect as a given amount of silver sulphide. Our data on the kinetics of the reactions show conclusively that the reaction with sulphite is the slower. This is confirmed by analyses of the emulsions. Nonhalide silver, determined by the modified Weigert and Lühr method, is again indicated by the numbers in the circles locating experimental points, in figures 5 and 6. These indicate that about 1 percent of the sulphite reacted with the silver bromide at the most (assuming that the nonhalide silver in the undigested portions was there before addition of the sulphite). If this is correct, silver is equivalent to a larger amount of silver sulphide [4] rather than a lesser one. For either sensitizer the optimum amount of nonhalide silver present as sensitivity nuclei in our emulsions is about 1 to 5×10^{-5}, expressed in terms of its atomic ratio to silver halide. This is toward the lower limit of Sheppard's estimate (14).

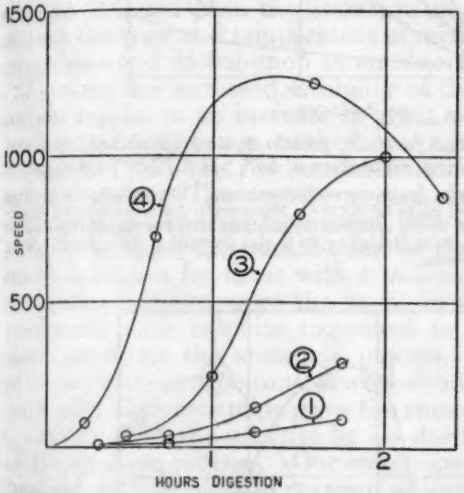

FIGURE 4.—*Emulsions made by the C-1 formula, gelatin 1, and sensitized by digestion with sodium sulphite after washing, in vacuum at 55°, pH 6.8 [Br] 3-5×10⁻⁵.*

Ratio of sodium sulphite to silver bromide in terms of chemical equivalents. Curve 1, 0; curve 2, 5×10^{-4}; curve 3, 1.3×10^{-3}; curve 4, 2.4×10^{-3}. That is, the sulphite added to the emulsion giving curve 4 was sufficient to reduce 2.4 atoms of silver per 1,000 from silver bromide to metallic silver.

The sensitivity of the emulsion passes through a maximum on continued digestion with sulphite, as in other methods of after-ripening. The height of the maximum is roughly constant over a moderate range

[4] The nonhalide silver in the emulsions made with deactivated gelatin and sensitized with either allylthiocarbamide or sodium sulphite was less than in emulsions made with active gelatin (27).

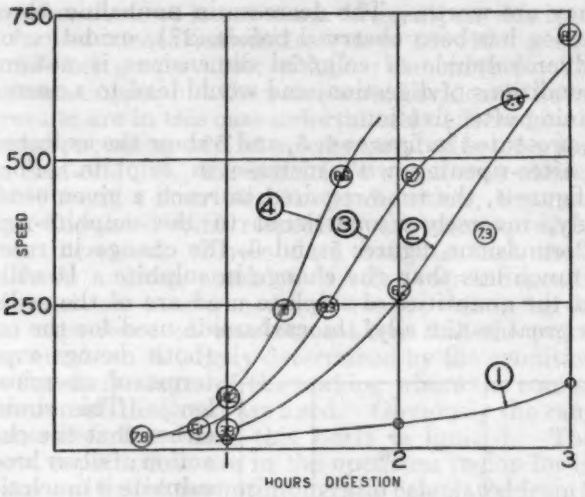

FIGURE 5.—*Emulsion made by the C-2 formula, gelatin 2, and sensitized by digestion with sodium sulphite after washing, in beakers at 55°*, pH *6.7* $[Br^-]$ 1.3×10^{-4}.

Curve 1, control emulsion digested under same conditions without sulphite. Ratio of sulphite to silver bromide: Curve 2, 1.9×10^{-3}; curve 3, 3.8×10^{-3}; curve 4, 7.6×10^{-3}. Numbers in the circles locating experimental points give the nonhalide silver found in the emulsion by analysis after the digestion indicated by the location of the point; these numbers are to be divided by 10^3 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

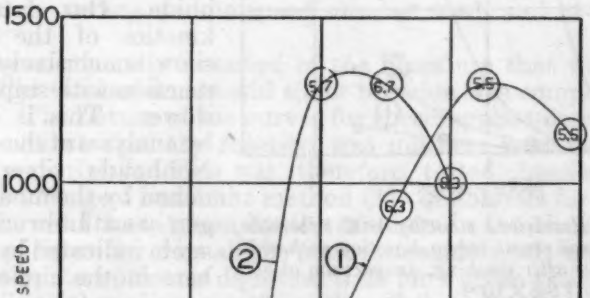

FIGURE 6.—*Emulsion made by the C-2 formula, gelatin 2, and sensitized by digestion with sodium sulphite after washing, in vacuum at 55°*, pH *7.4* $[Br^-]$ 5×10^{-4}.

Ratio of sulphite to silver bromide: Curve 1, 1.5×10^{-3}; curve 2, 6×10^{-3}. Numbers in the circles locating experimental points give the nonhalide silver found by analysis in the emulsion after the digestion indicated by the location of the point; these numbers are to be divided by 10^3 to give the ratio of the nonhalide silver to silver bromide in terms of chemical equivalents.

of conditions; ratios of sulphite to silver bromide of 1.5×10^{-3} or over appeared to differ mainly in the rate of change (figures 6 and 10 show well-defined maxima with different concentrations). Using the same formula, the maximum obtainable with sulphite was slightly lower than that with allyl thiocarbamide; the difference in the numerical values used for plotting the curves was very small, but it was larger on the basis of $10/i$. The results with these two essentially different sensitizers are still close enough to emphasize that the maximum sensitivity is determined more by the composition, structure, and size of the grains than by the subsequent ripening processes.

Results with the C-1 and C-2 formulas are parallel. A number of experiments were made with emulsions of pure silver bromide or with 1 percent AgI. Such emulsions have less capacity for sensitization, as judged from experience with after-ripening under normal conditions (27) and from the literature on emulsions. It is necessary to adjust the time and temperature of mixing in order to secure the same grain size and distribution in emulsions with varying iodide content (27), since the increased solubility of the silver halide with decreasing iodide results in an increase in grain size if the formula is otherwise unchanged. This was worked out quite well for the emulsions with 1 percent AgI; the few emulsions made with pure bromide had a coarser grain. The results proved difficult to reproduce and the experiments were not completed, but it was evident that under the same conditions the sensitization of these emulsions by sulphite was much less than for those with 4 to 5 percent AgI, and that the pure-bromide emulsions were the worse in this respect. Our earliest experiments with sulphite happened to be with pure-bromide emulsions made by the ammonia process. In these, increases in speed of 50 percent over the control were obtained; comparative experiments with allyl thiocarbamide gave the same results.

Oxidation of the sulphite by air during digestion is a complication of the ripening process. Our emulsions are normally digested in open beakers with stirring to prevent settling; the exposed surface is large enough so that the liquid may be expected to be saturated with air. The effect of the aerial oxidation is apparently less than would be expected, most probably because adsorption of the sulphite to silver bromide protects it. Comparative results of digestion with and without exclusion of air are given in figure 7. Digestion in vacuum was accomplished by pouring the freshly melted emulsion into a balloon flask provided with a special low-sulphur stopper [6] through which was run a stopcock. The flask was evacuated repeatedly, usually with small additions of alcohol, until the froth was broken and the warmed emulsion boiled vigorously under the reduced pressure. The sulphite solution was then introduced through the stopcock without breaking the vacuum. The samples for coating were removed by inverting the flask over a bottle with a 2-hole stopper, through which the stopcock passed tightly, evacuating the bottle and opening the stopcock when the pressure was below the vapor pressure in the flask. The flask was shaken violently before taking a sample, or every half hour if the sampling was less frequent; settling was negligible. Comparing curve 1 with curve 2, and curve 3 with curve

[6] We are indebted to the rubber section of this bureau for making these stoppers; comparison of control batches digested in flasks fitted with them with those digested in the usual way demonstrated that they did not cause fog or sensitization.

4, the indications are that the loss of sulphite by oxidation was relatively small. The rate of after-ripening in vacuum was definitely faster in curve 4 than in curve 3; in this emulsion 4-127, the concentration of sulphite was less than in 4-124, curves 1 and 2, so that the effect of oxidation might be larger. Curves 1 and 2 might legitimately be drawn in practical coincidence, although the form chosen for curve 2 is the most probable considering its points alone. Later experiments were generally made in vacuum, although in some cases, which are indicated, the open beakers were used for convenience. It was later decided to make experiments with more careful exclusion of oxygen. In these, the same apparatus was used as for the vacuum digestion, but the flask was repeatedly evacuated and flushed out with nitrogen or hydrogen. Digestion under hydrogen was found to

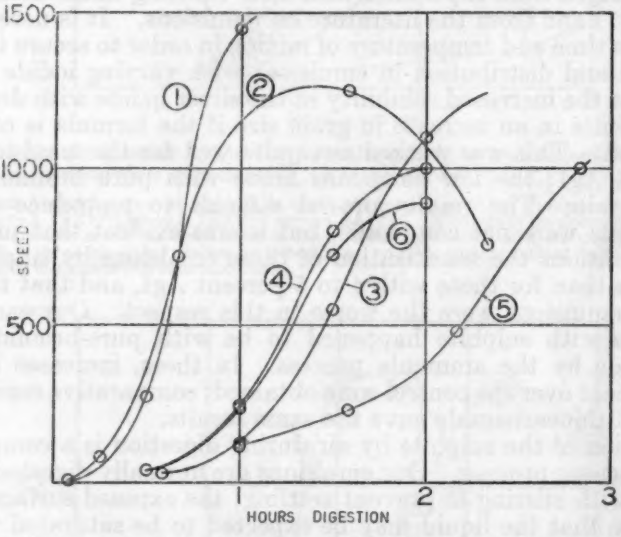

FIGURE 7.—*Comparison of sensitization of emulsions digested with sulphite after washing with and without free access of air.*

Curves 1 and 2, emulsion 4-124, C-1 formula, gelatin 1; digested at 55° pH 6.8 [Br⁻] 5.6×10^{-4}, sulphite-silver bromide ratio 2.4×10^{-3}; curve 1 in beaker, curve 2 in evacuated flask. Curves 3 and 4, emulsion 4-127, C-1 formula, gelatin 1; digested at 55°, pH 6.7, [Br⁻] 2.9×10^{-4}, sulphite-silver bromide ratio 1.3×10^{-4}; curve 3 in beaker, curve 4 in evacuated flask. Curve 5, emulsion 4-180, C-1 formula, gelatin 2; digested at 55°, pH 6.5 [Br⁻] 2.6×10^{-4}, sulphite-silver bromide ratio 1.5×10^{-3} in evacuated flask. Curve 6, emulsion 4-186; conditions identical with 4-180 except that flask was filled with nitrogen.

cause heavy fog, accompanied by an increased rate of after-ripening in the early stages of the process. It was at first thought that this indicated extensive oxidation of the sulphite even in the vacuum digestion, but direct comparison with nitrogen proved that the fog came from the hydrogen.[6] It is possible that the colloidal silver formed by the sulphite catalyzed further reduction of the silver bromide by the hydrogen. Curves 5 and 6 compare the digestion of C-2 emulsions in vacuum and nitrogen; the other halves of these emulsions were digested under hydrogen. The results indicate a considerable oxidation of the sulphite in the vacuum run, but are less reliable because curves 5 and 6 are for different emulsions.

[6] Both gases were freed from oxygen by passing slowly through a spiral wash bottle filled with fresh alkaline pyrogallol.

6. FOG AND STABILITY OF SULPHITE-SENSITIZED EMULSIONS

Fog densities corresponding to the maximum sensitivities shown in the figures were from 0.06 to 0.13 corrected for the density of the support. The fog densities of emulsions sensitized with allyl thiocarbamide to the same range of sensitivity fell within the same range; using active gelatins, the values were about the same for the best samples. It is a distinct practical advantage for the sulphite that the effect of concentration is not so critical as with other sensitizers. For example, the longest time of digestion of emulsion 4-178 with the higher concentration, 6×10^{-3}, was ⅛ more than the optimum, and the decrease in sensitivity was about ¼; the corresponding fog was only 0.21. Under corresponding conditions with thiocarbamide or active gelatin, the fog has usually been 0.3 to 0.4.

Adding the amounts necessary to give a reasonable digestion time, only a small percentage of the sulphite is utilized, so that it was feared that the plates would fog rapidly on storage. This has not been the case; the stability has been rather better than normal on the plates which have been tested. The tests were made after 1 year storage, repeating the Eder-Hecht wedge exposure used for the preliminary test, with tank development in pyro giving fog about the same as 6-minute brush development. Fog densities after 1 year for the plates corresponding to the maximum speeds on the curves are as follows: Figure 4, curve 3, fog 0.21; figure 4, curve 4, fog 0.18; figure 7, curve 1, fog 0.14; figure 10, curve 4, fog 0.27. Speed was in all cases constant as closely as could be determined by Eder-Hecht exposures. These are satisfactory values after 1 year in the climate of Washington. In all 4 cases cited, the emulsion had been given a thorough washing, digested, and coated without addition of soluble bromide, the bromide-ion concentration being 2 to $3\times10^{-5}N$. For practical use, bromide would have been added after digestion in the ratio of about 3 KBr:1,000 AgBr, raising the bromide-ion concentration to 5 to 8×10^{-4} N; this would avoid the edge fog which was obvious for a few mm from uncut edges of the plates, as well as increasing the time of stability. The unexpectedly high stability is probably explained by oxidation of the sulphite by air during drying which eliminates the excess sensitizer. Analytical data in proof of this have not been obtained, as time was not available to attempt a test of such obvious difficulty.

7. HYDROGEN-ION CONCENTRATION

The rate of after-ripening with sulphite is less sensitive to hydrogen-ion concentration than the corresponding process in active gelatin; the data in figure 8 illustrating the variation with pH may be compared with the corresponding figures 2 and 3 of B.S. Research Paper No. 430. Control batches for each value of pH have been included in figure 8, as the activity of treated gelatins has been found to be liable to be highly dependent on this variable. The data on sulphite sensitization which are illustrated were obtained by vacuum digestion. Two sets of experiments by digestion in beakers gave results less dependent on pH and falling in no regular order, although in both cases the batch at 6.7 gave a minimum rate. The most probable

explanation of this behavior lies in competition for the sulphite between the silver bromide and the oxygen of the air; oxidation by the air being highly dependent on hydrogen-ion concentration, the reaction between silver bromide and sulphite might actually assume a minimum at some pH. Our data show no indication of systematic

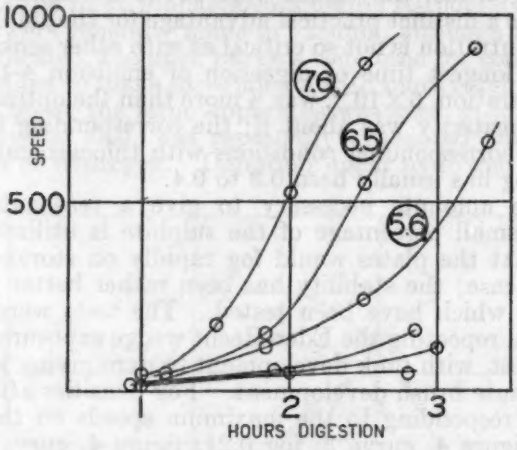

FIGURE 8.—*Comparison of sensitization of emulsion digested with sodium sulphite in vacuum after washing, at varying* pH.

Emulsion 4-177, C-2 formula, gelatin 2; [Br^-] as washed 4.6×10^{-4}. Numbers on the curves indicate pH of digestion. The lower curves are for digestion of a control emulsion without sulphite at the same values of pH.

difference in the maximum sensitivity obtainable at different hydrogen-ion concentrations within the range tested.

8. BROMIDE-ION CONCENTRATION

After-ripening with active gelatin or with pure sensitizers such as allyl thiocarbamide is retarded by increase in bromide-ion concentration, but the sensitivity reaches its maximum value by digestion at a bromide-ion concentration which may be as high as 1×10^{-3} N (27). Since bromide ions are also a product of the ripening with sulphite, similar relations may be expected to hold. Data obtained with C-2 emulsions are presented in figure 9, those from C-1 emulsions in figure 10. The reaction rate is more sensitive to bromide-ion concentration than to hydrogen-ion concentration, but the factor is less than 2 as far as it can be estimated from the time required to reach a given sensitivity. Neither approaches the effect of the concentration of sulphite; the time for a given effect was not more than doubled when the bromide-ion concentration was multiplied by 10. The effect of bromide-ion concentration on the sulphite sensitization is at least as large as on the corresponding process with allyl thiocarbamide, and is much greater than when sodium thiosulphate or active gelatin is used (27). Contrary to the case of normal after-ripening (with active gelatin), the maximum sensitivity is not improved by addition of soluble bromide to a thoroughly washed emulsion before digestion; with sulphite the more rapid after-ripening led to results which were always as good and in some cases better. This may possibly be

explained by the oxidation of sulphite by air from leakage into the flask with consequent serious loss before the end of a long digestion, but it seems more likely to be characteristic of the process. As bromide may be added after digestion as a preservative, it is obviously

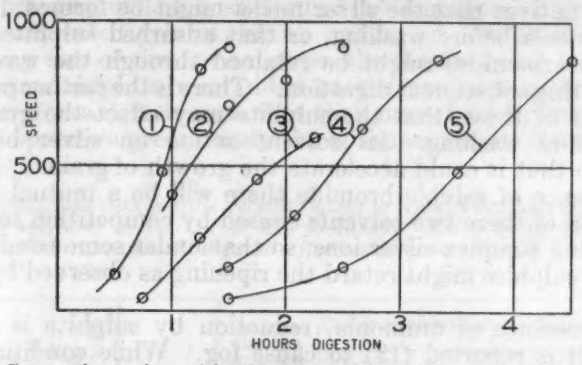

FIGURE 9.—*Comparison of sensitization of emulsions digested with sodium sulphite after washing in vacuum at varying bromide-ion concentrations.*

Curves 1 and 3, emulsion 4-194, C-2 formula, gelatin 2 pH 6.7, sulphite-silver bromide ratio 3.0×10^{-3}. curves 2, 4, and 5, emulsion 4-179; digested under same conditions except pH 7.7. Bromide-ion concentrations [Br⁻]: Curve 1, 3.1×10^{-4}; curve 2, 1.0×10^{-4}; curve 3, 2.6×10^{-4}; curve 4, 1.2×10^{-4}; curve 5, 4.8×10^{-4}.

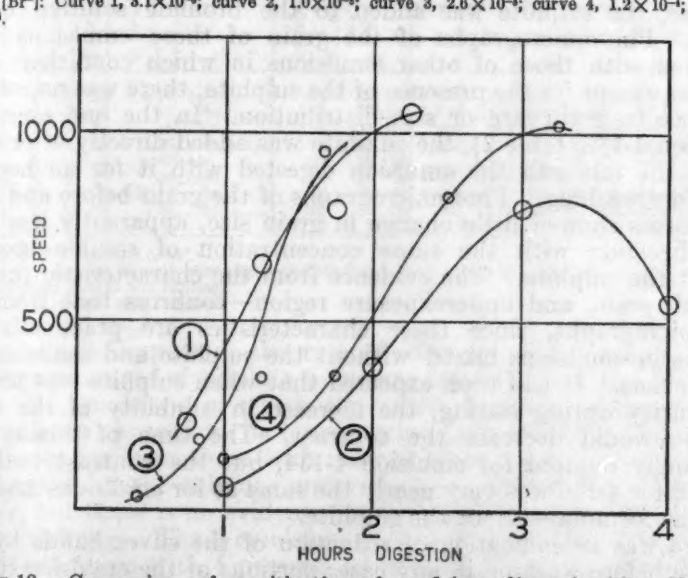

FIGURE 10.—*Comparison of sensitization of emulsions digested with sodium sulphite after washing at varying bromide-ion concentrations.*

Emulsion 4-140, C-1 formula, gelatin 1; digested in beakers at 55°, pH 6.6, sulphite-silver bromide ratio 3×10^{-3}; curve 1, [Br⁻] 3.1×10^{-4}, curve 2, 9.4×10^{-4}. Emulsion 4-134, C-1 formula, gelatin 1; digested in evacuated flasks at 55°, pH 6.5, sulphite-silver bromide ratio 1.3×10^{-3}; curve 3 [Br⁻] 1.5×10^{-4}, curve 4, 2.4×10^{-4}.

better practice to digest the emulsion after thorough washing ([Br⁻] around 2×10^{-5}) and add the preservative before coating.

9. EMULSIONS WITH SULPHITE ADDED BEFORE WASHING

Most of the experiments were made by the additions of sulphite to the washed emulsion, since this permitted control of the sulphite concentration and made the observation of its effect simpler than when

change in grain size or other processes may be taking place. For practical use, it might be preferred to add the sulphite to the emulsion before washing (although on washing with hard water there might be difficulty with precipitation of calcium sulphite). There would then be the alternatives that the silver nuclei might be formed during the ripening process before washing, or that adsorbed sulphite (like adsorbed thiocarbamide) might be retained through the washing and function during subsequent digestion. There is the further possibility, independent of these, that the sulphite may affect the grain size if present before washing. Its solvent action on silver bromide is sufficient so that it could accelerate the growth of grains. However, in the presence of soluble bromide there will be a mutual reduction in the action of these two solvents caused by competition to form the corresponding complex silver ions, so that under some conditions the addition of sulphite might retard the ripening as observed by Valenta (18).

In the presence of ammonia, reduction by sulphite is relatively rapid and it is reported (13) to cause fog. While conditions might be adjusted to avoid this, the limited number of experiments which we were able to make were all with neutral emulsions, appropriately modified from the type formulas given on page 747. In all but one case, the sulphite was added to the bromide solution before mixing. Photomicrographs of the grain of these emulsions were compared with those of other emulsions in which conditions were the same except for the presence of the sulphite; there was no evident difference in grain size or size distribution. In the one exception (emulsion 4-138, table 2), the sulphite was added directly after completing the mix and the emulsion digested with it for an hour at 65° before washing. Photomicrographs of the grain before and after this process showed little change in grain size, apparently less than from digestion with the same concentration of soluble bromide without the sulphite. The evidence from the characteristic curve—contrast, scale, and underexposure region—confirms that from the photomicrographs, since these characteristics are practically the same as in emulsions mixed without the sulphite and sensitized by other means. It had been expected that when sulphite was present in quantity during mixing, the increase in solubility of the silver bromide would decrease the contrast. The time of mixing was accordingly reduced for emulsion 4-134, but the contrast both for this and for 4-136 was very nearly the same as for emulsions made by the same formula without the sulphite.

There was no indication of reduction of the silver halide by the sulphite before washing in any case; portions of the emulsion coated without digestion were invariably of low sensitivity, practically indistinguishable from controls. In the case of emulsions 4-189 and 4-190, the excess of bromide over silver had been reduced so that the bromide-ion concentration was only 5.6×10^{-3} N after adding all the silver solution. During addition of the secondary gelatin before chilling, the emulsions were held at 65° C., pH 7.3 and the above bromide-ion concentration for 10 minutes, but the undigested emulsions were as insensitive as others with more bromide and less sulphite. It is probable that continued digestion under these conditions would have produced some sensitization. While we were unable to test this, there is little reason to expect that the results

would be superior to those which we obtained by digestion of the emulsions after washing. In this case, the after-ripening is best explained by adsorbed sulphite left after washing. A less probable hypothesis, concerning which we have no evidence, is that some new sensitizing compound has been formed by digestion of the sulphite with the deactivated gelatin during mixing of the emulsion. The after-ripening was of the normal type, the results being very similar to those where sulphite was added to the emulsion after washing. The nature of the data is such that they must be tabulated, and for economy of space we present only the optimum results for each digestion.

TABLE 2.—*Emulsions with sodium sulphite added to bromide solution before mixing. Volumes of solutions as for C-1 or C-2 formulas. Mixed in 26–29 minutes at 65° except as otherwise stated; digested after washing at 55°, pH 7.1±0.3, [Br^-] $2.5\pm1\times10^{-3}$*

Emulsion number	Gelatin	Percent AgI	Percent excess NH_4Br	G equivalents Na_2SO_3 per g equivalent AgBr	Digestion conditions	Optimum digestion time, minutes		Characteristics at digestion time nearest optimum								
								Speed						γ			Fog
								$10/E_m$			10/1						
						Interpolated	Nearest experimental value	3	6	12	3	6	12	3	6	12	6
4-188	2	4	25	0.10	Air	95	90	330	770	920	320	370	315	0.57	0.90	1.33	0.05
4-189	2	4	2	.10	do	100	90	290	740	1,400	245	230	230	.61	.94	1.42	.10
4-193	2	5	25	.15	do	120	115	155	500	690	200	315	250	.46	.64	.95	.02
4-196[a]	2	5	25	.15	Vacuum	100	90	460	950	1,400	630	620	500	.41	.70	1.16	.09
4-190	2	4	2	.40	Air	35	30	315		1,150	260	260	390	.54	.82	1.19	.26
4-136	1	4	10	.50	do	35	30	730	1,380	1,500	630	490	415	.50	.90	1.29	.11
4-138	1	4	25	[b]0	do	65	60	480	1,150	1,100	640	730	480	.40	.64	.95	.08
4-134[c]	1	4	10	.50	do	80	80	180	330	470	100	100	100	1.06	1.61	2.20	.09

[a] Mixed at 70° C. instead of 65°.
[b] No sulphite in mix; directly after mix added Na_2SO_3 in 0.50:1 ratio and digested 1 hour at 65° before adding secondary gelatin and chilling.
[c] Mixed in 14 instead of 26 minutes.

As would be expected, the rate of after-ripening increased with increasing amounts of sulphite (compare 189 with 190, and 188 with 136). The emulsions in which the excess bromide in the original mix had been reduced to its lowest value (189 and 190) had appreciably more fog than those with normal excess bromide; an increase in adsorption of the sulphite under these conditions is theoretically possible, but there is no evidence for it in the form of increased rate of after-ripening. The 2 emulsions with 5 percent AgI after-ripened slower than those with 4 percent, as is to be expected. Indications from the results with emulsions 4-193 and 4-196 are that still faster emulsions might have been obtained by increasing the amount of sulphite in the same basic formula.

Results with emulsions of this type were quite similar to those when the sulphite was added after washing. This process might be preferred for practical use. As already stated, the digestion could probably be eliminated by using a small excess of soluble bromide in the original solutions and ripening after mixing, but this is less likely to be satisfactory than the after-ripening.

This type of formula appears to have the practical disadvantage of less stability on storage. After 1 year, the fog was about 1.0

for emulsions 4-134 and 4-136, and 0.6 for 4-138. Data on the others are not available; the fog may be expected to be less in those with less sulphite. These values could undoubtedly be much reduced by adding bromide before coating.

The experiments completed were all made with deactivated gelatin in order to study as simple a system as practicable. The important practical question of the combination of sulphite with a gelatin having normal activity was not covered. A few data were obtained on the related question of the sulphite content of emulsion gelatins. Three gelatin samples which had recently been tested in the C-1 formula were analyzed for SO_2 by the method of Poetschke (34); this procedure, based on weighing $BaSO_4$ derived from oxidation of volatile material by iodine, should be free from positive errors caused by the presence of other compounds in gelatin. The results were, respectively, 0.11, 0.15, and 0.007 percent SO_2. Correlation between SO_2 content and photographic characteristics of gelatins obviously should not be attempted without a large number of samples, and might then be impossible without analysis for other variables with an accuracy not now available. In the C-1 formula, the above amounts would correspond to ratios of 10, 13, and 0.3×10^{-3} g equivalent of SO_2 to 1 of AgBr. In this formula, where all the gelatin is added before washing, such amounts of SO_2 would be negligible. If, however, gelatin were added after washing, as in many formulas, the ratio with the second of these gelatins might reach 4×10^{-3} under conditions which would make its effect quite appreciable. Whether it would be desirable or undesirable would obviously depend on conditions in the emulsion, as it might lead either to increased sensitivity or to the increase in fog and decreased sensitivity characteristic of excessive amounts of sensitizer. Sheppard (35) mentions sulphur dioxide as undesirable in photographic gelatins to which dyes are to be added, but makes no specific reference to any effect on the emulsion. Wentzel (36) and Wall (20) list it as an undesirable impurity, placing the limit at 0.01 percent and 0.1 percent, respectively, without giving reasons for this limitation. The lower limit is to be recommended on the grounds of reproducibility of results with the gelatin, but attention should be called to the possibility of sensitization by amounts which are to be found in emulsion gelatins.

10. EXPERIMENTS WITH OTHER REDUCING AGENTS

It is obvious that other reducing agents might be found which would satisfy the condition of forming a molecular compound or complex ion with silver salts. A low rate of reaction is probably a further requirement for sensitization. Experiments were made with only two other materials: hydrazine and sodium arsenite. These were added to portions of an emulsion in amounts sufficient to reduce 1 atom of silver per 1,000, and digested with it at 55°, pH 6.5, $[Br^-]$ 2×10^{-5}. The hydrazine produced neither sensitization nor fog in 2 hours. The sodium arsenite in the same time produced an increase over the control which was close to the limit of error.

III. CONCLUSIONS

The data presented in this paper appear to be adequate proof that metallic silver may function as sensitivity nuclei. Silver is very probably formed during digestion with active gelatin; if formed it may increase sensitivity and the results with sulphite indicate, but do not prove, that it does.

The analytical results must be used with some caution but they indicate that the quantity of the nonhalide silver is not satisfactorily related to its sensitizing effect and that, therefore, part of it fails to function as sensitivity nuclei. Chemically equivalent amounts of silver and silver sulphide appear to have roughly the same sensitizing effect. The evidence is not sufficient to decide whether the superior results obtainable with allyl thiocarbamide are to be ascribed to the formation of silver sulphide or to the mechanism of the reaction by which it is formed. Sulphites fall into the same class with the other nuclear sensitizers in that they form a molecular complex with silver salts. Further investigation of reducing agents as sensitizers is desirable to establish how general this rule may be.

The relatively high concentration of sulphite necessary to produce a given rate of reaction, and the marked effect of bromide-ion concentration on the rate, are both in accordance with the low reduction potential of the sulphite. The effect of hydrogen-ion concentration is of the right order of magnitude for any oxidation-reduction reaction.

While many of the emulsions sensitized with sulphite were of commercial quality, none were equal to the best obtainable by standard methods from the same type formulas. The experiments which have been made by no means exhaust the possibilities of improvement. In general, the best results were obtained by rapid after-ripening, with high pH and low bromide-ion concentration; as there was little tendency to cause fog, the digestion could be carried out in this way, and the emulsion then stabilized by addition of soluble bromide and possibly acid with little loss of sensitivity. The presence of sulphur dioxide in emulsion gelatins assumes a new importance since, under certain circumstances, it may cause sensitization as well as fog.

IV. ACKNOWLEDGMENTS

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CONSISTENCY OF POTATO-STARCH SIZE [1]

By Walter T. Schreiber, M. N. V. Geib, and O. C. Moore

ABSTRACT

The physical characteristics imparted to cotton-warp yarn in the so-called "slashing" or sizing operation are dependent in part upon the consistency of the starch size used in the processing. In textile mill practice, the size is heated and agitated from the time it is prepared until it is consumed. The potato-starch sizes, however, are more or less unstable, and continuous heating and agitation tends to cause a decrease in the consistency of the size.

Laboratory experiments show that the decrease in consistency of size is dependent upon the temperature of cooking, speed of agitation, and length of the cooking period.

It seemed reasonable to suppose that the decrease in consistency of sweetpotato-starch size may be due to the catalytic action of liquefying enzymes of amylase which may be present in the starch. Although various treatments calculated to remove or destroy such enzymes failed to stabilize the consistency, the addition of a solution containing small quantities of dispersed lecithin and lanum to the sweetpotato-starch size materially retarded the decrease in consistency. The reason for this action is not yet clear.

The consistency of sweetpotato-starch size can be greatly increased by washing the starch with certain simple solutions.

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I. INTRODUCTION

Starch is used extensively in the textile industry for sizing warp yarns. This is done to increase the abrasive resistance of the yarns, to give them added body, and to increase their weight.

In mill practice this sizing operation is carried out in a "slasher." In this machine, the yarns are first passed through a vat containing a hot suspension of starch in water, called the "size", pressed between rollers, and dried by passing over or around one or more steam-heated cylinders. A starch pot for preparing the size and storage tanks for the latter complete the slasher equipment. The pot and tanks are equipped with both open and closed steam coils and agitators.

The size is prepared by cooking and agitating a mixture of starch and water, either with or without other ingredients, until the starch is thoroughly gelatinized and a uniform mixture is obtained. This mixture is then transferred to the storage tank where it is held at

[1] This study was carried out in the laboratories of, and in cooperation with, the Alabama Polytechnic Institute, Auburn, Ala. The Carbohydrate Division of the Bureau of Chemistry and Soils in the U.S. Department of Agriculture also cooperated in providing some of the sweetpotato starch used in this work.

constant temperature by heating with steam and is agitated to maintain uniform concentration. From the storage tank the size is either added continuously to the sizing vat as fast as it is consumed in the process or it is circulated from the storage tank through the sizing vat and back to the storage tank. The size is thus heated and agitated from the time it is prepared until it is consumed. The physical characteristics of sized yarn are materially affected by the consistency

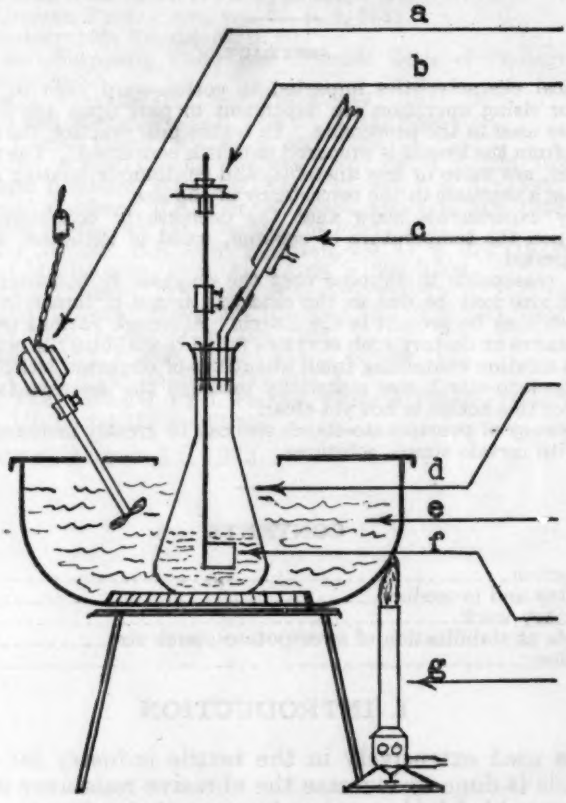

FIGURE 1.—*Starch paste apparatus*

a=Oil stirrer
b=Pulley
c=Water condenser
d=Erlenmeyer flask (200 cc)
e=Oil bath
f=Starch paddle
g=Burner

of the size.[2] This consistency decreases (the solution gets thinner) markedly with prolonged heating and stirring,[3] particularly when noncereal starches are used; and since, in commercial practice, as explained above, it is customary to subject the size to prolonged heating and agitation, it follows that the maintenance of uniform quality in the sized yarn is difficult, if not impossible.

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The purpose of the present study was to determine the effect of different variables on the consistency of potato-starch size, and, if possible, to find some means of preventing or decreasing the change in consistency under the above conditions.

II. APPARATUS AND PROCEDURE

The conditions encountered in mill practice were simulated, as far as practicable, in the apparatus used for the experimental cooking. This is shown diagramatically in figure 1. With this set-up it was possible to regulate the temperature as well as the rate of agitation, and thus to reproduce any given cooking conditions.

The general procedure was as follows: A sample of starch equivalent to 4.5 g of bone-dry material was placed in a 200 ml Erlenmeyer flask with 100 ml of distilled water and immersed in the heated-oil bath. The paddle was operated at 150 r.p.m. and the oil bath was

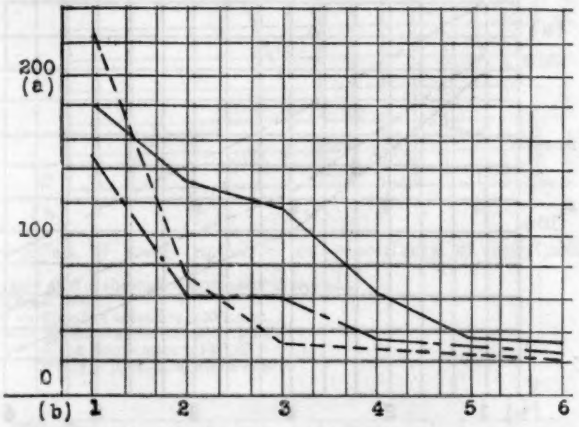

FIGURE 2.—*Effect of time of cook on consistency of starch sizes*

(a) = Time of flow of 20 cc through viscosimeter in seconds
(b) = Time of cook, hours
———— Sweetpotato starch (A.P.I.)
– – – – Irish-potato starch
—·—·— Sweetpotato starch (Dept. of Agriculture)
Cook temperature, 105° C.
Speed of agitation, 150 r.p.m.
Time of cook, 1, 2, 3, 4, 5, and 6 hours.

maintained at 105° C. throughout the cooking, except as otherwise indicated. The temperature of the mixture inside the flask was approximately 5° C. lower than that of the oil bath, but the temperature of the oil bath is the one shown on the curves.

To determine the so-called consistency of the size, a Saybolt viscosimeter[4] was used. During the determination the temperature of the viscosimeter was held at 95° C.[5] The times required for 5, 10, 15, and 20 ml of size to flow through the orifice were observed, but it was sufficient to use only the last as a measure of the consistency.

III. PRELIMINARY WORK

A series of preliminary experiments was carried out, the results of which are shown graphically in figures 2 to 5, inclusive.

[4] Twenty-six seconds were required for 60 cc of distilled water to flow through the viscosimeter at a temperature of 95° C.
[5] This temperature was used in all determinations throughout this investigation.

Figure 2 shows the effect of prolonged cooking on the consistency of various starches. Three different starches were used in these experiments, namely, a sweetpotato starch made at the Alabama Polytechnic Institute, Auburn, Ala., designated A.P.I.; another sweetpotato starch made by the Carbohydrate Division of the Bureau of Chemistry and Soils, United States Department of Agriculture, and an irish-potato starch. The temperature of the oil bath, the speed of agitation, and the concentration of the size were uniform throughout this series. Determinations of consistency were made at 1-hour intervals over a 6-hour cooking period. The results show that prolonged heating causes a decided decrease in the consistency of all the samples and that the rate of this breakdown varies with the individual starches and is slowest with sweetpotato size.

The effect of different cooking temperatures on the consistency of three samples of sweetpotato-starch size is shown in figure 3. The

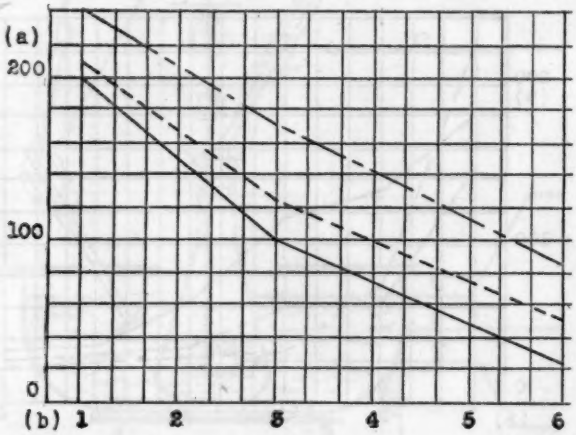

FIGURE 3.—*Effect of temperature of cook on consistency of sweetpotato-starch size*

(a) = Time of flow of 20 cc through viscosimeter in seconds
(b) = Time of cook, hours
———— Cook temperature, 105° C.
– – – – Cook temperature, 95° C.
—·—·— Cook temperature, 90° C.
Speed of agitation, 150 r.p.m.
Time of cook, 1, 3, and 6 hours.

speed of agitation and the concentrations of the mixtures were kept uniform in these runs, while the temperature of the oil bath was maintained at 105°, 95°, and 90° C., respectively. Determinations of consistency were made at the end of 1, 3, and 6 hours of cooking. The results show that the higher temperatures produce a size of lower consistency.

Figure 4 shows the effect of agitation during the cooking period on the consistency of sweetpotato-starch size. The samples, each 4.5 g of A.P.I. sweetpotato starch plus 100 ml of water, were cooked at an oil-bath temperature of 105° C, with the speeds of agitation maintained at 150 and 270 r.p.m., respectively. Consistency determinations were made at 1-, 3-, and 6-hour intervals over a 6-hour cooking period. These determinations apparently show that after gelatinization of the starch has been brought about, the more severe agitation during cooking causes a more rapid decrease in the consistency of the size.

The effect of age of the sweetpotato starch on the consistency of size made therefrom is shown in figure 5. Batches of size were made from the same sample of starch at 6-month intervals during 18 months.

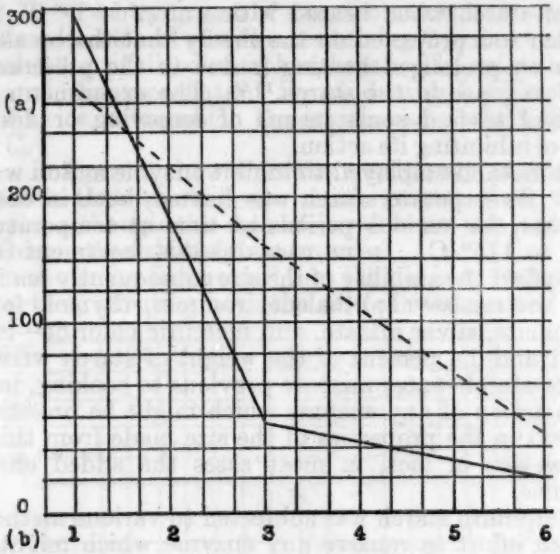

FIGURE 4.—*Effect of severe agitation on consistency of sweetpotato-starch size*

(a) Time of flow of 20 cc through viscosimeter in seconds.
(b) Time of cook, hours.
– – – – Speed of agitation, 150 r.p.m.
———— Speed of agitation, 270 r.p.m.
Cook temperature, 105° C.
Time of cook, 1, 3, and 6 hours.

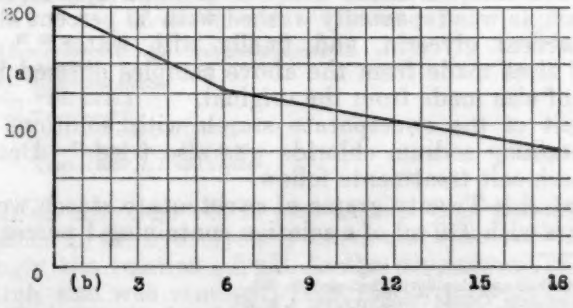

FIGURE 5.—*The consistency of starch size made from sweetpotato starch aged for various time periods*

(a) Time of flow of 20 cc through viscosimeter in seconds.
(b) Aging periods, months.
Rate of agitation, 150 r.p.m.
Cook temperature, 105° C.
Time of cook, 3 hours.
Determinations at 0, 6, 12, and 18 months.

The data show that in the case of this particular lot of sweetpotato starch the consistency of the size decreased as the age of the starch increased.

IV. ATTEMPTS AT STABILIZATION OF SWEETPOTATO-STARCH SIZE

There seems to be no generally accepted theory regarding the behavior of starch when heated with water.[6] [7] [8] [9] [10] [11] The present investigation was projected on the theory that the breakdown of the starch size on prolonged heating is due to the presence of a small amount of amylase in the starch.[12] [13] The experiments were therefore designed to find some means of removing or destroying this enzyme or of inhibiting its action.

The first method employed to inhibit enzyme action was the use of heat.[14] [15] [16] Sweetpotato starch was heated, both in the dry and in the wet state, for various periods of time at temperatures ranging from 105° to 175° C. In no case did this treatment of the starch materially affect the stability of the size subsequently made therefrom.

Various materials—naphthalene, resorcin, thymol, formaldehyde, copper sulphate, silver nitrate, and mercuric chloride—in concentrations of 0.1 and 0.4 percent of the weight of starch were added to a sweetpotato-starch-water mixture previous to cooking, in an effort to inhibit the action of any enzyme which might be present.[17] [18] [19] No improvement in the properties of the size made from this starch was noted, however; in fact, in most cases the added chemical made matters worse.

The sweetpotato starch was subjected to various methods of purification in an effort to remove any enzyme which might be present. The first treatment consisted of washing the sweetpotato starch successively with sulphurous acid (having a pH value of 2.6) and water; then with a 0.5 percent solution of sodium hydroxide, followed again by water; with acetic acid (having a pH of 2.8); and finally with water. Samples were taken after each water wash. In another set of experiments the original starch was washed with saturated solutions of calcium carbonate and trisodium phosphate, respectively. Another sample was repeatedly washed with 50 percent alcohol, then with 10 percent glycerin, and finally with water.[20] [21] The consistency of sizes made from the above samples differed but slightly from that of size made from the original.

Treatment of the sweetpotato starch with solutions of soluble starch containing sodium chloride was also tried.[22] Details of two typical starch-salt treatments follow.

Treatment A.—Twenty grams of sweetpotato starch were agitated for 1.5 hours with 250 ml of a solution containing 1 percent of soluble

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[20] Sherman and Schlesinger, J.Am.Chem.Soc. vol. 37, p. 643, 1915.
[21] Thorpe, Dictionary of Applied Chemistry, vol. 3, p. 131.
[22] Ambard, Amylase, Its Estimation and Mechanism of Its Action, Bull. Soc. Chim. Biol. vol. 3, pp. 51-65, 1921.

starch and 0.5 percent of NaCl. The mixture was allowed to settle, and the liquid decanted. This treatment was repeated three times and the resulting starch was finally washed with water, filtered, and dried at 50° C.

Treatment B.—Twenty grams of sweetpotato starch were agitated for 40 minutes with 300 ml of water containing 6 g of rice starch, 0.6 g of NaCl, and 1.2 g of disodium phosphate. The mixture was then centrifuged and the supernatant liquid decanted. This treatment was repeated twice, after which the starch was washed, filtered, and dried at 50° C.

The curves in figure 6 show that the consistency of sizes obtained from the starch thus treated was much greater than that of the control sample, although the rate of breakdown was not materially affected. This method shows great promise.

It has been shown by Sorensen [23] that the pH is an important factor in enzymic action, affecting both the rate of reaction and the rate of

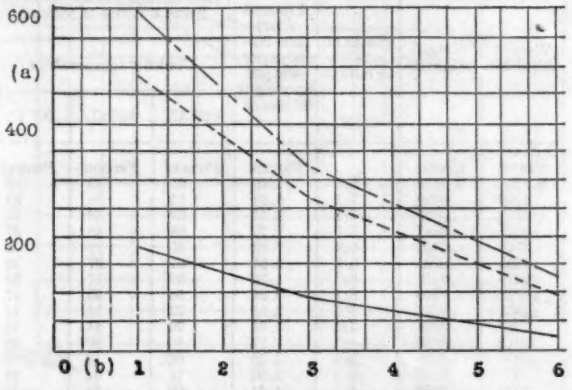

FIGURE 6.—*Effect of consistency of sweetpotato-starch size of treatment with solutions of soluble starch and certain salts*

(a) = Time of flow of 200 cc through viscosimeter in seconds.
(b) = Time of cook, hours.
——— Untreated starch.
– – – – Treatment A.
— - — Treatment B.
Cook temperature, 105° C.
Speed of agitation, 150 r.p.m.
Time of cook, 1, 3, and 6 hours.

inactivation of enzymes. It is also known that the acidity has a direct influence on the hydrolysis of starch and other carbohydrates.

Accordingly the relation of pH to the consistency of the sweetpotato starch size was studied. The starch mixtures consisted of 95 ml of water, 5 ml of a buffering solution prepared according to McIlvaine [24], and 4.5 g of starch. Buffering solutions having pH values of 3, 4, 5, 6, 7, and 8 were used. The addition of the buffer solutions, however, did not appreciably retard the breakdown of the sweetpotato starch during the cooking operation.

Sueyoski and Aoke [25] report that colloidal solutions of lecithin inhibit the action of amylase, and Truszkowski [26] says that amylase is absorbed by lipoids.

[23] Sorensen, Bio. Chem. Zeitsch., vol. 22, p. 352, 1910; vol. 21, pp. 131, 279, 1909.
[24] Clark, The Determination of Hydrogen Ions, p. 116.
[25] Sueyoski and Aoke, Influence of Lipoids, Phospholipins on Action of Enzymes, Sei-ipkawi Med. J., vol. 48, no. 8.
[26] Truszkowsky, Structure of Enzyme Action, Bio. Chem. J., vol. 22, pp. 767-72.

These claims suggested the use of cholesterol (lanum) and lecithin in the size mixtures, as possible inhibiting agents.

The lecithin-lanum solutions were prepared by adding a given weight of lecithin to a measured volume of distilled water and vigorously agitating with a high-speed mixer at a temperature of 50° C. After the lecithin was thoroughly dispersed, a given weight of lanum was added and the solution again thoroughly mixed. Definite volumes of these solutions were added to the starch sample (4.5 g) and distilled water was added to make the total volume of the mixture 100 ml. This mixture in turn was cooked as indicated in table 1, which gives data showing the effect of these reagents on the stability of sweetpotato-starch size.

TABLE 1.—*Effect of various cooking temperatures on sweetpotato starch to which small quantities of lecithin[a] and lanum[b] have been added*

Weight of lecithin	Weight of lanum	Ratio of lecithin to lanum	Amount of lecithin-lanum as percentage by weight of starch	Loss of consistency between 3 and 6 hours of cooking		
				Cooking temperature		
				105° C.	95° C.	90° C.
Grams	*Grams*		*Percent*	*Percent*	*Percent*	*Percent*
0.1355	0.0170	8:1	3.39	61	40	11
.2710	.0380	7:1	6.89	52	38	25
.1355	.0193	7:1	3.44	62	32	15
.0677	.0097	7:1	1.72	68	48	27
.2710	.0450	6:1	7.02	35	28	3
.1355	.0225	6.1	3.51	61	27	10
.0677	.0112	6:1	1.75	68	51	20
.2710	.0540	5:1	7.24	58	30	17
.1355	.0275	5:1	3.62	73	15	14
.0677	.0125	5:1	1.81	70	44	16
.2710	.0680	4:1	7.52	46	30	30
.1355	.0338	4:1	3.76	60	19	5
.0677	.0170	4:1	1.88	71	61	34
.1355	.0450	3:1	4.01	60	33	13
No addition (4.5 g starch per 100 ml water).....				74	60	45

[a] Lanum, anhydrous lanolin.
[b] Lecithin, commercial grade recovered from soybean.

Figure 7 shows the effect of lecithin and lanum on the consistency of a sweetpotato-starch size, as compared with that of the original starch. One hundred ml of a lecithin-lanum solution were prepared containing 0.271 g of lecithin and 0.045 g of lanum. This solution was cooked with 4.5 g of sweetpotato starch at 90° C. over a 6-hour period. Consistency determinations were made at 1- 3- and 6-hour intervals. The blank was made from 4.5 g of starch and 100 ml of water under the same conditions.

These data show conclusively that colloidal solutions of lanum and lecithin added to sweetpotato size retard the breakdown of the size, especially at the lower cooking temperatures. The reason for this action is not yet understood.

V. DISCUSSION

This study shows that size from sweetpotato starch is in many ways similar to that from irish-potato starch, although it has several individual characteristics. Both starches, when made into size, seem

to reach a maximum consistency during the early part of the cooking period, and gelatinization appears to be complete at this time; upon further cooking the consistency decreases until a minimum or water-like consistency is reached. The change in consistency appears to be slower in sweetpotato-starch sizes than in those from irish-potato starch.

The latter is widely used in the textile industry as a sizing material and sweetpotato starch seems to have similar possibilities. The elimination, even partially, of the change in the consistency of potato-starch sizes would increase their value.

The present investigation has shown that this object can be attained in part at least, in the case of sweetpotato-starch size by the addition of lecithin and lanum. Further investigation may show other materials to be even more suitable for this purpose, especially from an

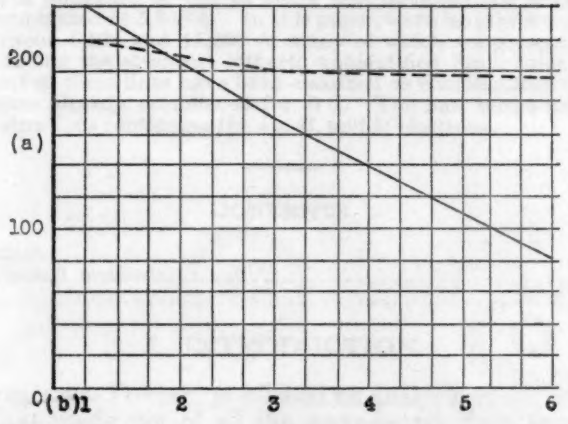

FIGURE 7.—*Effect of addition of lecithin-lanum on consistency of sweetpotato-starch size.*

(a) =Time of flow of 200 cc through viscosimeter in seconds
(b) =Time of cook, hours
———— No addition to sweetpotato-starch size
– – – – Lecithin-lanum added to sweetpotato-starch size
Cook temperature, 90° C.
Speed of agitation, 150 r.p.m.
Time of cook, 1, 3, and 6 hours

economic viewpoint. The present cost of lecithin and lanum would probably limit their use as sizing ingredients. The prices of commodities, however, are not fixed and if larger consumption were assured lower prices might follow.

The important practical conclusions from this work are that the consistency of sweetpotato-starch size can be greatly increased (two fold to threefold) by washing with certain simple solutions, and that the breakdown of the size on heating can be considerably retarded.

Acknowledgment is hereby made to Edward Wolesensky for suggestions on the work and for assistance in the preparation of this paper for publication.

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ARC SPECTRUM OF SILICON IN THE RED AND INFRARED

By C. C. Kiess

ABSTRACT

No accurate description of the red and infrared portion of the arc spectrum of silicon has been published in the 40 years that have elapsed since Rowland's work which terminated at 5,948 A. In this paper, wave lengths are given for 130 new lines between 6,125 and 11,290 A, many of which are present in the solar spectrum, including the strongest hitherto unidentified Fraunhofer line. More than 50 percent of these lines have been classified as combinations between new terms and terms already established for Si I. The new terms arise from the electron configurations containing the $4p$, $4f$, and $5f$ electrons.

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I. INTRODUCTION

Several years ago Fowler [1] published an analysis of the arc spectrum of silicon that made use of all the wave-length data then available and gave additional wave lengths down to 1590 A in the extreme ultraviolet. From this work, which gave the salient features of the term structure of Si I, it appears that no extension of our knowledge of the spectrum has been made into the red and infrared beyond the longest wave length, 5,948.5 A observed by Rowland 40 years ago.[2] However, Fowler's analysis indicated that several groups of prominent lines were to be expected in this region. It is true that McLennan and Shaver [3] published a list of red and infrared lines purporting to be characteristic of the arc spectrum of silicon, but none of them, except possibly three, appear to belong to this element.

Exploration of the arc spectrum of silicon into the red and infrared, as far as photographic methods would permit, was begun more than 17 years ago at the Bureau of Standards. The material used as electrodes in the arc was fused silicon, about 90 percent pure, in the form of rough lumps. However, this material emitted the spectra of iron, titanium, vanadium, zirconium, calcium, barium, and other impurities, with such prominence that only a few of the remaining unidentified lines could, with certainty, be ascribed to silicon. These were identified with solar absorption lines by Meggers [4] in his extension of the sun's spectrum to 9,000 A.

[1] Proc. Roy. Soc. (London), vol. A, 123, p. 422, 1929.
[2] Phil. Mag., Series 5, vol. 36, p. 49, 1893.
[3] Trans. Roy. Soc. (Canada), series III, vol. 18, p. 21, 1924.
[4] Publ. Allegheny Observatory, vol. 6, p. 13, 1919.

In the meantime, our knowledge of spectra in the red and near infrared has increased to such a state of completeness that it is now possible to eliminate from an unknown spectrum the lines due to the metallic impurities in the source. Furthermore, with a fairly complete term analysis of a spectrum, such as Fowler has made for Si I, it is possible to test new lines for their relationship with it.

The discovery, about 2 years ago, at the Eastman Kodak Laboratories, of new photo-sensitizing materials that have greatly extended the range and increased the speed of plates suitable for infrared photography, has made it desirable to examine again the spectrum emitted by silicon in this region. The properties of these new sensitizers, named mesocyanin and xenocyanin, have been described by Mees.[5] They have their maximum sensitizing power at 8,600 and 9,700 A, respectively, but xenocyanin is effective throughout a broad band extending from 9,000 to nearly 12,000 A.

II. APPARATUS AND METHODS

The observations were made with two grating spectrographs equipped with 21-foot concave gratings, ruled with 7,500 and 20,000 lines per inch, and a plane grating ruled with 20,000 lines per inch. The three instruments give dispersions in the first order spectrum of 10.4, 3.5, and 2.7 A/mm, respectively. For wave lengths longer than 9,000 A only the spectrograph with the small dispersion was used; for wave lengths shorter than 9,000 A all three instruments were used. In every case, exposures to the silicon arc were accompanied by exposures to the iron arc to furnish standard wave lengths in either the first or second order for use in the wave length determinations.

The light source was the arc in air between lumps of the same fused silicon as was used in the work of 17 years ago. The arcs carried currents ranging from 6 to 16 amperes supplied by 220-volt dc mains. It was found that, with lumps of silicon weighing 10 g or less and with currents under 10 amperes, it was necessary to restrike the arc every minute or two. With heavier lumps, 50 g or more in weight, the arcs burned steadily for periods up to one half or three fourths hour. Craters of glassy silica formed over the surface of the electrodes so that when the arc went out, it could not be struck again until the glaze was broken off.

As stated above, all the recent observations have been made on the new types of plates produced by the Eastman Kodak Laboratories. Before exposure, the plates were hypersensitized in an ammonia bath, then rinsed in alcohol, and dried rapidly in a current of air. To record the silicon arc spectrum as tabulated below, exposure times ranging from 1 to 4 hours were required. The plates were measured and reduced according to our usual practice, the reference lines of the iron arc being those adopted as secondary standards by the International Astronomical Union.[6] No measurements of the lines between 3,905 and 5,948 A appear to have been made on the international wave-length scale since those of Fowler,[7] who

[5] J. Optical Soc. Am., vol. 21, p. 753, 1931; vol. 22, p. 204, 1932; vol. 23, p. 229, 1933.
[6] Trans. Internat. Astron. Union, vol. 3, p. 77, 1928.
[7] Phil. Trans. Roy. Soc. (London), vol. A 225, p. 1, 1925.

reported three new lines in the yellow. These lines have been remeasured on the high-dispersion plates made in this investigation and the results, incorporated in table 1, are described below.

III. RESULTS

The new wave lengths of the silicon arc spectrum are given in table 1. Most of the lines are not sharp and some are asymmetrical, being shaded toward the red or the violet. These qualities are indicated in the second column of the table by the letters, *h*, *l*, and *v*, respectively, following the intensity. The letter *b* indicates a broadening of the line, which, however, is not sufficient to impart the appearance of diffuseness. All the other lines are sharp.

Comparison of the wave lengths of table 1 with the solar lines in the Revision of Rowland's Preliminary Table[8] and with Babcock's list of Temporary Standards in the Infrared Solar Spectrum[9] shows that all the intense silicon lines, and many of the fainter ones, are in the sun's spectrum. These include the line at 6,155 A, the strongest hitherto unidentified solar line. In general, the laboratory wave lengths are longer than the solar values. For the lines in the yellow, which are relatively sharp and can be measured more accurately than the diffuse and unsymmetrical red lines, the mean shift is +0.04 A. For the red lines it is +0.12 A. Part of these shifts may be the result of pressure and probably Stark effects in the source, the arc in air; but in the case of the red lines the measurements are affected in many instances by blending of strong multiplet lines with very close and fainter satellites. The wave lengths of the infrared lines beyond 10,000 A are systematically shorter than the solar lines by 0.06 A. These lines were measured only on plates taken with the low-dispersion grating and the difference between their wave lengths and the solar values may be accounted for by difference in scale between the two sets of measurements.

TABLE 1.—*Wave lengths in the arc spectrum of silicon*

NOTE.—The angstrom. In view of the present unanimous agreement and general practice in expressing optical wave lengths in terms of the so-called "international angstrom" the Bureau of Standards considers the time opportune to represent the international angstrom by the abbreviation A. Where the Rowland scale of wave lengths is intended it should be clearly specified as such.

The "angstrom" as at present used was defined and adopted in 1907 by the International Union for Cooperation in Solar Research (now the International Astronomical Union) and also adopted in 1928 by the International Conference on Weights and Measures. The angstrom is equal to 1/6438.4696 of the wave length of cadmium red radiation, and within the limits of the most refined measurements of Michelson, and of Fabry, Perot, and Benoit, this value of the angstrom is identical with the definition 1 angstrom $= 10^{-10}$ meter.

[8] Carnegie Institution of Washington, Publication no. 396, 1928.
[9] Trans. Internat. Astron. Union, vol. 4, p. 83, 1932.

λ_{air} A.	Intensity	ν_{vac} cm^{-1}	Term combinations
11, 290. 02	0	8, 854. 95	
11, 187. 75	1	8, 935. 90	
11, 018. 02	7	9, 073. 59	$4s^3P_2^3$—$4p^3D_2$
10, 982. 40	1	9, 102. 98	
10, 979. 27	10	9, 105. 60	$4s^3P_2^3$—$4p^3P_1$
10, 885. 23	2*b*	9, 184. 25	
10, 882. 58	1*b*	9, 186. 48	
10, 869. 50	50	9, 197. 54	$4s^1P_1^1$—$4p^1D_2$
10, 843. 98	15*b*	9, 219. 19	$4s^3P_1^1$—$4p^3P_0$
10, 827. 06	50	9, 233. 59	$4s^3P_2^3$—$4p^3P_2$
10, 786. 81	25	9, 268. 05	$4s^3P_1^1$—$4p^3D_2$
10, 784. 02	2	9, 270. 44	
10, 749. 32	35	9, 300. 36	$4s^3P_1^1$—$4p^3P_1$
10, 727. 17	30*b*	9, 319. 57	$4s^3P_2^3$—$4p^3D_3$
10, 694. 14	25*b*	9, 348. 35	$4s^1P_1^1$—$4p^1P_1$
10, 689. 56	20*b*	9, 352. 36	$4s^3P_0^3$—$4p^3D_1$
10, 660. 94	40	9, 377. 47	$4s^3P_0^3$—$4p^3P_1$
10, 627. 76	15*b*	9, 406. 74	
10, 603. 37	50	9, 428. 39	$4s^3P_1^3$—$4p^3P_2$
10, 585. 08	100	9, 444. 67	$4s^3P_2^3$—$4p^3S_1$
10, 499. 00	2	9, 522. 10	
10, 371. 25	50	9, 639. 40	$4s^3P_1^1$—$4p^3S_1$
10, 288. 93	25	9, 716. 52	$4s^3P_0^3$—$4p^3S_1$
10, 155. 88	1	9, 843. 81	$4p^3D_3$—$5d^3D_3^3$
10, 100. 84	1	9, 897. 45	
10, 067. 74	3	9, 929. 99	$4p^3P_2$—$5d^3D_3^3$
10, 020. 16	1	9, 977. 15	$3d^1D_2^2$—$5p^3P_1$
10, 015. 33	1	9, 981. 96	
10, 009. 82	1	9, 987. 45	
9, 967. 46	1	10, 029. 90	
9, 913. 05	1	10, 084. 95	$4p^3P_2$—$6s^3P_1^1$
9, 891. 92	5*b*	10, 106. 49	$4p^3S_1$—$6s^3P_2^3$
9, 886. 82	2*b*	10, 111. 71	
9, 839. 40	2*b*	10, 160. 44	$4p^3P_1$—$6s^3P_1^1$
9, 789. 16	2*h*	10, 212. 58	$4p^3P_1$—$6s^1P_1^1$
9, 770. 10	4*b*	10, 232. 51	$4p^3D_3$—$6s^3P_2^3$
9, 768. 20	5*b*	10, 234. 51	$4s^3P_2^3$—$4p^1D_2$
9, 757. 84	2*h*	10, 245. 36	$4p^3D_2$—$6s^3P_0^3$
9, 738. 48	6*b*	10, 265. 73	$4p^1S_0$—$7s^1P_1^1$
9, 689. 38	8*b*	10, 317. 75	$4p^3P_2$—$6s^3P_2^3$
9, 627. 00	1	10, 384. 61	$4s^3P_2^3$—$4p^1P_1$
9, 585. 80	2	10, 429. 24	$4s^3P_1^1$—$4p^1D_2$
9, 505. 25	2	10, 517. 69	
9, 413. 54	100	10, 620. 08	$4s^1P_1^1$—$4p^1S_0$
9, 318. 35	3	10, 728. 57	
9, 254. 62	4*h*	10, 802. 47	$3d^3P_2^2$—$5f^3F_3$
9, 238. 87	2*h*	10, 820. 86	
9, 208. 70	7*b*	10, 856. 32	
9, 022. 38	2*h*	11, 080. 50	
9, 008. 90	5*h*,*l*	11, 097. 09	$3d^3P_2^2$—$5fX_2$
8, 949. 34	15*b*	11, 170. 95	
8, 925. 52	8*b*	11, 200. 76	
8, 899. 50	3*b*	11, 233. 51	
8, 898. 97	3*b*	11, 234. 18	
8, 892. 96	25*b*	11, 241. 77	
8, 883. 87	4*b*	11, 253. 27	
8, 791. 28	5*b*	11, 371. 79	
8, 790. 88	4*b*	11, 372. 30	
8, 790. 53	6*b*	11, 372. 76	
8, 752. 16	200	11, 422. 62	$3d^1D_2^2$—$4f^3F_2$
8, 742. 57	100	11, 435. 15	$3d^1D_2^2$—$4f^3F_3$
8, 728. 98	5*b*	11, 452. 95	

λ_{air} A.	Intensity	ν_{vac} cm^{-1}	Term combinations
8, 728. 36	10*b*	11, 453. 76	
8, 648. 54	100*h*,*l*	11, 559. 47	
8, 597. 15	2*h*,*l*	11, 628. 57	
8, 556. 63	100*h*	11, 683. 64	$3d^1D_2^2$—$4f^3D_2$
8, 555. 52	2*h*	11, 685. 15	$3d^1D_2^2$—$4f^3D_3$
8, 536. 45	3*b*	11, 711. 26	
8, 503. 13	1*b*	11, 757. 15	
8, 502. 33	10*b*	11, 758. 25	$3d^1D_2^2$—$4fX_3$
8, 501. 48	3*b*	11, 759. 43	$3d^1D_2^2$—$4f^3D_1$
8, 444. 01	5*b*	11, 839. 46	$3d^1D_2^2$—$4fX_2$
8, 230. 64	7	12, 146. 39	$3d^3D_3^3$—$5p^3P_2$
8, 211. 38	2	12, 174. 88	$3d^3D_2^2$—$5p^3P_2$
8, 093. 32	25*b*	12, 352. 47	
8, 035. 35	7*b*	12, 441. 59	
8, 025. 73	3*b*	12, 456. 50	
8, 025. 42	4*b*	12, 456. 98	
8, 007. 46	3*b*	12, 484. 93	
7, 970. 91	3*b*	12, 542. 18	
7, 970. 25	10*b*	12, 543. 21	
7, 952. 46	3*b*	12, 571. 27	
7, 943. 91	500	12, 584. 80	
7, 932. 14	250	12, 603. 48	
7, 918. 37	200	12, 625. 39	
7, 913. 49	10*b*	12, 633. 18	
7, 912. 55	3*b*	12, 634. 68	
7, 850. 93	2*h*	12, 733. 85	
7, 801. 30	3*h*	12, 814. 86	
7, 800. 68	4*h*	12, 815. 87	
7, 743. 84	4*h*	12, 909. 94	
7, 743. 14	4*h*	12, 911. 11	
7, 680. 48	100*b*	13, 016. 44	
7, 424. 70	20	13, 464. 86	$3d^3D_3^3$—$4f^3F_3$
7, 423. 64	500	13, 466. 78	$3d^3D_3^3$—$4f^3F_4$
7, 416. 08*	250	13, 480. 50	$3d^3D_2^2$—$4f^3F_2$
7, 409. 14	100	13, 493. 13	$3d^3D_3^3$—$4f^3F_3$
7, 405. 94	300	13, 498. 96	$3d^3D_1^1$—$4f^3F_2$
7, 289. 28	250	13, 715. 00	$3d^3D_3^3$—$4f^3D_3$
7, 275. 24	50	13, 741. 47	$3d^3D_2^2$—$4f^3D_2$
7, 250. 74	40*b*	13, 788. 09	$3d^3D_3^3$—$4fX_3$
7, 235. 98	5*b*	13, 816. 03	$3d^3D_3^3$—$4fX_3$
7, 235. 30	10	13, 817. 32	$3d^3D_2^2$—$4f^3D_1$
7, 226. 20	10	13, 834. 73	$3d^3D_1^1$—$4f^3D_1$
7, 208. 28	1*b*	13, 869. 12	$3d^3D_2^2$—$4fX_2$
7, 193. 64	6*b*	13, 897. 34	$3d^3D_2^2$—$4fX_2$
7, 184. 94	7*b*	13, 914. 17	$3d^3D_1^1$—$4fX_2$
7, 167. 47	3*h*	13, 948. 08	
7, 165. 78	50*h*,*l*	13, 950. 98	$3d^1D_2^2$—$5f^3F_{3,2}$
7, 035. 25	50*b*	14, 210. 22	$3d^1D_2^2$—$5f^3D_2$
7, 017. 81	10*h*,*l*	14, 245. 54	$3d^1D_2^2$—$5fX_2$
7, 005. 73	50*h*,*v*	14, 270. 11	
7, 003. 67	50*h*	14, 274. 30	
6, 976. 80	10*h*	14, 329. 27	
6, 255. 60	3*h*	15, 981. 26	$3d^3D_3^3$—$5f^3F_3$
6, 254. 55	15*h*,*l*	15, 983. 95	$3d^3D_3^3$—$5f^3F_4$
6, 245. 11	2*h*	16, 008. 11	$3d^3D_3^3$—$5f^3F_3$
6, 244. 74	12*h*	16, 009. 06	$3d^3D_2^2$—$5f^3F_2$
6, 238. 42	4*h*	16, 025. 27	$3d^3D_1^1$—$5f^3F_2$
6, 156. 00	10*h*	16, 239. 83	$3d^3D_3^3$—$5f^3D_2$
6, 155. 32	50*h*	16, 241. 62	$3d^3D_3^3$—$5f^3D_3$
6, 145. 22	15*h*	16, 268. 32	$3d^3D_2^2$—$5f^3D_2$

* This line appears to be complex on some plates, but is not sufficiently resolved to permit measurement of the components.

λ_{air} A.	Intensity	ν_{vac} cm^{-1}	Term combinations
6, 142. 70	6*h*	16, 274. 99	$3d^3D_3^0$—$5fX_3$
6, 132. 14	4*h*	16, 303. 02	$3d^3D_2^0$—$5fX_2$
6, 131. 60	5*h*	16, 304. 45	$3d^3D_2^0$—$5f^3D_1$
6, 125. 44	2*h*	16, 320. 85	$3d^3D_1^0$—$5fX_2$
6, 124. 85	5*h*,*l*	16, 322. 42	$3d^3D_1^0$—$5f^3D_1$
5, 948. 584	100	16, 806. 08	$4s^1P_1^0$—$5p^1D_2$
5, 797. 912	40	17, 242. 82	$4s^3P_2^0$—$5p^3D_3$
5, 793. 128	30	17, 257. 06	$4s^3P_1^0$—$5p^3D_2$
5, 780. 452	25	17, 294. 90	$4s^1P_1^0$—$5p^1S_0$
5, 772. 258	50	17, 319. 45	$4s^3P_0^0$—$5p^3D_1$
5, 754. 258	8*b*	17, 373. 63	$4s^3P_2^0$—$5p^3P_1$
5, 708. 437	75	17, 513. 08	$4s^3P_2^0$—$5p^3P_2$
5, 701. 138	25	17, 535. 50	$4s^3P_1^0$—$5p^3P_0$
5, 690. 470	40	17, 568. 38	$4s^3P_1^0$—$5p^3P_1$
5, 684. 523	50	17, 586. 76	$4s^3P_2^0$—$5p^3S_1$
5, 665. 601	25	17, 645. 49	$4s^3P_0^0$—$5p^3P_1$
5, 645. 665	25	17, 707. 80	$4s^3P_1^0$—$5p^3P_2$
5, 622. 22	3	17, 781. 64	$4s^3P_1^0$—$5p^3S_1$
4, 102. 926	25	24, 366. 00	$3p^1S_0$—$4s^3P_1^0$
3, 905. 527	100	25, 597. 52	$3p^1S_0$—$4s^1P_1^0$

The classified lines of table 1 arise from combinations of new terms with those of Fowler's 4*s*, 6*s*, 5*p*, and 3*p*′ groups. In table 2, which is abstracted from a similar table given by Fowler, are set forth the terms to be expected theoretically for the various electron configurations of the neutral silicon atom. Concerning the terms of the 4*p* group, he states that "the principal combinations . . . are outside the range of the observations in the infrared." These have now been established by the group of strong infrared lines between 10,000 and 11,000 A, representing the transition $4p \rightarrow 4s$. Only the terms $4p^1P_1$, $4p^3D_1$, and $4p^3P_0$ are uncertain, the others being verified through intersystem combinations or combinations with terms from the *ns* configurations.

TABLE 2.—*Theoretical terms of* Si I

Electron configuration	Terms of Si I with $^2P^0$ of Si II as limit
$3s^2.3p^2$	^3P, ^1D, ^1S
$3s^2.3p.ns$	$^3P^0$, $^1P^0$
$3s^2.3p.np$	^3D, ^3P, ^3S, ^1D, ^1P, ^1S
$3s^2.3p.nd$	$^3F^0$, $^3D^0$, $^3P^0$, $^1F^0$, $^1D^0$, $^1P^0$
$3s^2.3p.nf$	^3G, ^3F, ^3D, ^1G, ^1F, ^1D
$3s.3p^3$	$^3S^0$, $^3D^0$, $^3P^0$, $^1S^0$, $^1D^0$, ^1P

The $^3D^0$ and $^1D^0$ terms, which Fowler assigns to the sp^3 configuration, are involved in the production of some of the groups of diffuse lines that appear between 6,100 and 9,000 A. Many of the intense lines of these groups are separated by nearly the same wave-number differences as occur between the components of the $^3D^0$ term. The observations with the high dispersion spectrographs have shown that in reality these strong silicon lines are attended by much fainter, close satellites, thus indicating that the higher terms involved in their production have very narrow separations and arise from an s^2pf configuration. This view is supported by the fact that the new

terms are hydrogen-like in character, being closely represented by a Rydberg formula, as shown below. This suggests that the $^3D°$ and $^1D°$ terms owe their origin to the $3d$ electron, a possibility recognized by Fowler, who states, ". . . the $3p'$ and $3d$ terms yield similar combinations with the deep $3p$ terms, so that the $3p'$ terms might have been called $3d$, and subsequent d terms $4d$ and $5d$." The $3d$ configuration requires a $^3F°$ term in addition to $^3D°$, $^3P°$, and the corresponding singlet terms. Fowler's analysis of Si I does not give this term, although it should have a value of approximately 17,000 on his term scale. The parallel group of terms in Ge I has been assigned to the $4d$ electron by Rao [10] who has established the $^3F°$ term through its combination with the ground term $4p^3P$. Corresponding lines of Si I have not been found, although the ultraviolet from 1,950 A to 3,000 A has been resurveyed with the grating and Hilger E 1 spectrographs of the Bureau of Standards. Further attempts to establish the $^3F°$ term through its combinations with terms of the nf configurations have also proved unsuccessful, although it is probable that the strong, unclassified lines at 7,918, 7,932, and 7,943 A may represent its combination with $4f^3G$.

Fowler gives three terms, $^3D?$, ^3P and ^1S of the $5p$ configuration, of which ^3P is verified in this investigation, through its combinations with $3d$ $^3D°$ and $3d$ $^1D°$. It has not been possible to verify $^3D?$, in a similar manner. Prolonged exposures made with the large grating spectrographs and intended to bring out the satellite lines of its combination with $4s$ $^3P°$ likewise failed to verify the $5p$ ^3D term. However, the term fits satisfactorily into a Rydberg formula with $4p$ ^3D so that Fowler's estimate of it is very probably correct. It is of interest to note that faint, unidentified solar lines agree in wave length with the required satellite lines.

From the arrangement of the singlet terms in the $4p$ configuration, we may infer a similar arrangement for the corresponding singlet terms of the $5p$ configuration. This suggests that Fowler's term $5p$ $^1S_0$ is in reality $5p$ $^1D_2$. The unclassified yellow line at 5780.4 A may then be interpreted as the combination $4s$ $^1P_1^?$–$5p$ $^1S_0$ giving the value 7478.3 for the ^1S term. Although these terms are not verified through combinations with the $3d$ terms, yet evidence in support of their reality is furnished by the fact that they form Rydberg sequences with the $4p$ terms as shown in table 4. It has not been possible to establish the term $5p$ $^1P_1$.

On one of the strong grating exposures there appears a faint line at wave length 5,622.22 A, which is separated by 194.81 cm^{-1} from the unclassified silicon line at 5,684.52 A. This pair of lines may be interpreted as $4s$ $^3P_{2,1}^?$–$5p$ $^3S_1$, but no combinations of the new term, $5p$ ^3S, with other terms have been found to verify it. It is of interest, however, to note that a faint unidentified line appears in the solar spectrum at 5,622.237 A, which lends support to the view that the new line is related to the other yellow silicon lines, all of which are present in the sun's spectrum.

The new terms for Si I are given in table 3, which also gives corrections to some of Fowler's terms. The values of the terms are based on Fowler's scale, which is quite accurately determined, although some of his series now require revision. The designations of the new

[10] Proc. Roy. Soc. (London), A 124, p. 465, 1929.

terms of the *nf* configurations have been determined from their combinations with the 3*d* terms and from consideration of their behavior in forming series. Table 4 shows the effective quantum numbers or Rydberg denominators of the new terms. All the series are satisfactorily represented by the Rydberg formula with the exception of the *nf* $^3F_4$ terms, which, however, would satisfy the formula if their limit were $^2P_{1/2}$ instead of $^2P_{3/2}$ of Si II. In this case, the effective quantum numbers would be 3.9658 and 4.9604, respectively.

TABLE 3.—*New and revised terms of Si I*

Term type	ν	$\Delta\nu$	Term type	ν	$\Delta\nu$
$4p\ ^3P_0$	16, 785. 72		$4f\ ^3F_2$	6, 991. 25	
		81. 22			12. 58
$4p\ ^3P_1$	16, 704. 50		$4f\ ^3F_3$	6, 978. 67	
		128. 00			1. 91
$4p\ ^3P_2$	16, 576. 50		$4f\ ^3F_4$	6, 976. 76	
$4p\ ^3D_1$	16, 729. 69		$4f\ ^3D_1$	6, 654. 36	
		−7. 01			−75. 89
$4p\ ^3D_2$	16, 736. 70		$4f\ ^3D_2$	6, 730. 25	
		246. 16			1. 70
$4p\ ^3D_3$	16, 490. 54		$4f\ ^3D_3$	6, 728. 55	
$4p\ ^3S_1$	16, 365. 48		$4f\ X_3$	6, 655. 60	
$4p\ ^1D_2$	15, 575. 71		$4f\ X_2$	6, 574. 50	
$4p\ ^1P_1$	15, 425. 05		$5f\ ^3F_2$	4, 463. 73	
$4p\ ^1S_0$	14, 153. 32				1. 11
$5p\ ^3S_1$	8, 223. 27		$5f\ ^3F_3$	4, 462. 62	
$5p\ ^1D_2$	7, 967. 23				3. 02
$5p\ ^1S_0$	7, 478. 32		$5f\ ^3F_4$	4, 459. 60	
$6s\ ^3P_0$	6, 544. 10		$5f\ ^3D_1$	4, 166. 52	
		52. 35			−35. 18
$6s\ ^3P_1$	6, 491. 75		$5f\ ^3D_2$	4, 203. 60	
		233. 05			1. 62
$6s\ ^3P_2$	6, 258. 70		$5f\ ^3D_3$	4, 201. 98	
			$5f\ X_3$	4, 168. 42	

TABLE 4.—*Rydberg denominators*

Terms	$^3S_1$	$^3P_0$	$^3P_1$	$^3P_2$	$^3D_1$	$^3D_2$	$^3D_3$	$^1S_0$	$^1D_2$
3*p*		1. 2917	1. 2925	1. 2911				1. 4718	1. 3552
4*p*	2. 5670	2. 5508	2. 5630	2. 5510	2. 5610	2. 5605	2. 5575	2. 7566	2. 6301
5*p*	3. 5908	3. 5906	3. 6066	3. 5754	3. 5390	3. 5417	3. 5789	3. 7592	3. 6462

Terms	$^3D_1$	$^3D_2$	$^3D_3$	$^3F_2$	$^3F_3$	$^3F_4$	X_2
4*f*	3. 9760	3. 9547	3. 9547	3. 9618	3. 9652	3. 8866	3. 9902
5*f*	4. 9629	4. 9440	4. 9440	4. 9581	4. 9591	4. 8078	4. 9627

It remains to direct attention to some of the groups of unclassified silicon lines. The probable origin of the strong lines 7,918, 7,932, and 7,943 A was mentioned above. There are two other groups of diffuse lines which are apparently related through a common term involving the separations 106.5 and 81.1 cm^{-1}. The strongest lines of these groups are at 7,680.48 A and 8,648.54 A. Both appear as absorption lines in the sun's spectrum, although the former as a solar line, is much too strong to be due solely to manganese to which it is ascribed. In conclusion it may be pointed out that much yet remains to be found out about Si I, but that progress will most likely be made with a source different from the arc in air.

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CRITICAL STUDY OF THE DETERMINATION OF ETHANE BY COMBUSTION OVER PLATINUM IN THE PRESENCE OF EXCESS OXYGEN

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ABSTRACT

A sample of ethane of known purity was analyzed by the usual slow-combustion method; that is, over a hot platinum spiral in the presence of excess oxygen. The contraction after burning, the carbon dioxide produced, and the oxygen consumed were measured. The average results obtained from a series of 18 determinations indicated the impossibility of attaining the accuracies usually reported in the literature. The average volumetric equation for the reaction was $C_2H_6+3.5116\ O_2=1.9940\ CO_2+2.5190$ contraction. The weighted average equation was $C_2H_6+3.513\ O_2=1.994\ CO_2+2.520$ contraction. The contraction and oxygen consumed were invariably too high, and the carbon dioxide produced was invariably too low. The ethane was calculated from contraction, carbon dioxide, and oxygen separately and in various combinations, both uncorrected and corrected for deviations from theoretical molecular volumes. The average results from different methods of calculation varied from 99.13 percent to 100.76 percent. The best average value found by use of a single formula was 100.11 percent, and resulted from combining the contraction and carbon dioxide as one factor of an equation of which the other factor was oxygen. Such an equation eliminates part of the uncertainty concerning the proper method of correcting for deviation from theoretical molecular volumes. The averages of two pairs of formulas gave results very close to 100 percent. The ethane was also calculated on the assumption that methane, or propane, (known to be absent) was present. (The usual analysis would have been reported as methane and ethane.) Hydrocarbons other than ethane indicated by various methods of calculation from the average of the observed results varied from 0.3 percent of propane to 9.4 percent of methane.

A number of sources of error are discussed. These include small measured losses of ethane and carbon dioxide in the distributor, and a small loss of carbon dioxide by solution in the water produced by the combustion and otherwise present. Such errors must be present in every apparatus of this type, and will effect the analysis of all hydrocarbons to some extent. The observed results may be explained by correcting for these errors, and for the known deviation of carbon dioxide from its theoretical molecular volume with a similar correction for ethane, which is somewhat higher than the best estimated value available.

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I. INTRODUCTION

The direct method of attack in studying the real worth of any method of gas analysis is to use as the basic point of departure a gas of known purity. With such a material at command, the final destination is clear enough. If all the rules are observed en route, and the gas was definitely known at the start, the analytical results obtained are a measure of the value of the method. Unfortunately, no standard gas samples are available to the gas analyst, and perhaps this constitutes the only good reason why the obvious procedure has seldom been employed.

In the present work ethane of known purity was determined by combustion over heated platinum in the presence of excess oxygen. This established method is one of the most widely used in volumetric gas analysis. The accuracies which may be expected from it under the most favorable conditions of operation were thus determined directly for ethane. The errors which may explain the observed deviations from the theoretical result were of such a nature that they will affect the analysis of any hydrocarbon to some extent.

II. PURITY OF THE ETHANE USED

The ethane used in this series of determinations was a fraction separated from a West Virginia natural gas by the prolonged operation of a large rectifying column. It was stored in a 100-cubic-foot cylinder. The sample used for the determinations reported was drawn from the cylinder over mercury into a glass container. Air was excluded by flushing the sampling line with mercury, followed by a prolonged flushing with the sample, which in turn was transferred under measured positive pressure.

The purity of the ethane was studied in two ways: (1) by determining the ratio of carbon to hydrogen, and (2) by the differential vapor pressure method.

1. RATIO OF CARBON TO HYDROGEN

F. D. Rossini, of this Bureau, determined the ratio of carbon to hydrogen according to the method he employed for the methane used in his determination of the heat of combustion of this gas.[1] He reports these ratios as moles of hydrogen per 1.5 times the number of moles of carbon (or moles of water per 1.5 times the number of moles of carbon dioxide in the products of combustion) so that the ratio = 1 for pure C_2H_6. The values obtained are given (as reported) in table 1.

TABLE 1.—*Ratio of hydrogen to carbon in ethane used*

Date	Approximate amount burned (mole C_2H_6)	Mole H_2O per 1.5 moles CO_2	Mole H_2O/1.5 (moles CO_2) corrected for CO produced
Oct. 27, 1932	0.0675	1.00030	1.00010 } average, 1.0000±0.0002.
Oct. 29, 1932	.070	1.00002	0.99982 }
Dec. 2, 1932	.0284	.99944	0.99924 } average, 0.9993±0.0002.
Dec. 9, 1932	.049	.99955	0.99935 }

[1] F. D. Rossini, B.S. Jour. Research, vol. 6 (RP260), p. 37, 1931.

The ratios of the first series indicate pure ethane. The ratios of the second series indicate a change in composition which might be explained by a change in equilibrium between vapor and liquid phases within the storage cylinder. The impurity indicated could not be methane, but might be propane to the extent of 0.42 percent or ethylene to the extent of 0.21 percent. The method of establishing ratios of carbon to hydrogen takes no account of nitrogen or air.

2. DETERMINATION OF PURITY BY THE DIFFERENTIAL VAPOR PRESSURE METHOD

The sample used in the present work was drawn from the cylinder after the second series of the determinations of the ratio of carbon to hydrogen. Its purity was tested by the differential vapor pressure method previously suggested.[2] The vapor pressure of an initial distillate from the liquefied sample was compared with that of a middle cut and also against that of the final residue. The data are as follows: Approximately 1 liter of the sample was condensed at −190.3° C. The pressure above this condensate was 1.5 mm. The temperature was raised to −150° C.; the corresponding pressure was 7.5 mm. The condensate was distilled isothermally at this temperature until a few drops of distillate had collected at −190° C. on one side of the differential manometer, which was then closed. The distillation was continued until approximately half of the original condensate had vaporized; this portion was removed by a mercury vapor pump. The distillation was then continued until a few drops of distillate had collected at −190° C. in the opposite side of the differential manometer. The 2 condensation bulbs of the manometer were surrounded with frozen mercury to insure uniformity of temperature within both bulbs. The pressure of the initial distillate was observed to be 2.02 ± 0.03 mm greater than that of the middle fraction at a temperature of −190.3° C. The middle fraction was removed from the manometer and the distillation again continued until only a few drops of final residue remained. This residue was condensed in the side of the differential manometer previously containing the middle cut. The pressure of the initial distillate was observed to be 2.05 ± 0.03 mm greater than that of the final residue.

The conclusions are: (1) The sample of ethane contained a lower boiling impurity; (2) the sample contained no higher boiling impurity. (There are no known constant boiling mixtures which may have been involved.)

When the source and method of storing the sample are considered, the lower boiling impurities which may be expected, listed in the order of likelihood of occurrence, are methane or nitrogen or air, ethylene or helium. The latter two are not very likely to occur. If methane or ethylene were present in significant amounts, it would be possible to isolate fractions containing them by isothermal fractional distillation [2] of the condensate from which nitrogen had been removed. Accordingly, several days were devoted to a careful separation of a sample of the ethane, employing temperatures of −150° C. at the start and −170° C. at the end of the series of distillations. No increase of vapor pressure at corresponding temperatures

[1] Martin Shepherd, B.S. Jour. Research, vol. 2 (RP75), pp. 1156–7, and 1169–70, 1929.

was observed during these separations. It is accordingly safe to assume that lower boiling hydrocarbons were absent, or present in amounts so small as to be insignificant.

These observations indicate nitrogen or air as the most probable impurity. Assuming that nitrogen was present, we can make a rough calculation of the amount by using an equation derived by Washburn[3] from the laws of Raoult, Henry, and Dalton. If p_2 is the equilibrium pressure when the system is composed of a negligibly small quantity of vapor and a large quantity of liquid, p_1 the equilibrium pressure when the system is composed of a (negligibly) small quantity of liquid and a large quantity of vapor, K_B the Henry's law constant for the impurity B, and $\Delta = p_2 - p_1$, then X_B, the mole fraction of B in the mixture is given by the equation

$$X_B = \frac{K_B \Delta}{(p_2 - K_B)^2 + \Delta(2K_B - p_2)}.$$

In the present case, Δ has been directly measured by the differential manometer, and equals 2.02 mm. If the mixture is assumed to be an ideal solution, $K_B = p^\circ_B$, the vapor pressure of pure B (nitrogen), which is known to be close to 1370 mm at $-190°$ C. The value of p_2 need be known only roughly, and may be assumed to be 1.5 mm, the initial pressure upon condensation. Substituting these values in the above equation, and dropping factors of no significance,

$$X_B = \frac{2(1370)}{(1370)^2 + 2(2 \times 1370)} = 0.0015.$$

This figure would normally represent the mole fraction of nitrogen present in the total mixture, but in this instance the significance is different, since the initial condensate was actually obtained from a separation by distillation and not by a simple isothermal condensation. (This also accounts for the fact that Δ is greater than p_2.) If the separation was complete, it would follow that 0.0015 is the mole fraction of nitrogen in the initial distillate, and not in the entire mixture. Since the difference in purity between the initial distillate and the middle cut was the same as that between the initial distillate and the final residue, it is established that the separation of nitrogen was completed sometime before the middle cut was reached, and the maximum possible amount of nitrogen in the total mixture would be correspondingly reduced to approximately 0.0007. Furthermore, it is possible to compute the difference in purity between any two fractions. If p°_A and p°_B are the vapor pressures of the substances A and B in their pure states, and Δp is the difference in the vapor pressures of the two fractions or distillates, then the difference in purity, Δx_B, is given by the expression

$$\Delta x_B = \frac{\Delta p}{p^\circ_B - p^\circ_A}.$$

In the present case p_2 is negligible (<0.1) and Δp and p_2 have been measured or are known as noted before

$$\Delta X_B = \frac{2}{1370} = 0.0015$$

[3] E. W. Washburn, Constancy of Pressure During Isothermal Condensation or Vaporization as a Criterion for Purity, Zs. f. physik. Chem., Cohen Festband, p. 592, 1927.

This value checks the former computation of X_B for the mixture, and indicates that the separation of N_2 was completed with the initial distillation. Therefore 0.0015 mole fraction of nitrogen was present in the initial distillate alone. The order of magnitude of the nitrogen impurity may be calculated for the whole sample by assuming that the initial distillate did not comprise more than 10 percent of the total mixture. This assumption is more than safe, since only a few drops were observed from a total mixture of over 2 ml. Since the total volume of the gas sample was close to 1000 ml, the nitrogen impurity (using the above assumption) was $\frac{0.15}{1000} = 0.015$ percent or less.

3. ABSORPTION IN ALKALINE PYROGALLOL SOLUTION

The sample showed no measurable contraction after contact with potassium hydroxide solution or alkaline pyrogallol solution.

The conclusion is that the ethane used may be considered as pure for the purpose of this study. If the results of the analyses do not so indicate, the value of the analytical method has been measured. Since the analyses were performed carefully, and since both the apparatus and technic employed would eliminate many of the common errors often present in this general field of gas analysis, it is believed that the results are about as good as can be expected from the slow combustion of ethane.

III. APPARATUS AND METHOD OF ANALYSIS

1. APPARATUS

The standard apparatus for volumetric gas analysis previously described [4] was used. During part of the work, a U-tube of approximately 4 mm bore and 250 mm length was connected to the first 2 stopcocks of the distributor. This U-tube was filled with fresh ascarite and replaced the regular pipette containing potassium hydroxide solution. A water jacket surrounded the U-tube, and the temperature of the water was observed and compared with that of the water surrounding the burette. These observations were made during each measurement of a gas volume, and, together with the known capacity of the U-tube, served as a check against volumetric error from this source.

2. METHOD OF ANALYSIS

The analytical procedure was as follows. From 30 to 70 ml of nitrogen, obtained from the pipette containing alkaline pyrogallol solution, was measured and stored in the "pyro pipette", leaving the manometer and distributor filled with nitrogen and balanced at the pressure of the compensator. Approximately 90 ml of oxygen containing a known small percentage (0.76) of nitrogen was transferred to the burette, measured, and passed to the combustion pipette leaving the manometer balanced. A sample of approximately 20 ml of ethane was taken into the burette and measured. The gas over the mercury in the arm of the manometer connected to the distributor was taken into the burette. The pressures in the burette and combustion tube were independently adjusted to atmospheric. A

[4] Martin Shepherd, B.S.Jour. Research, vol. 6 (RP266), p. 121, 1931.

measured current was passed through the platinum spiral within the combustion pipette. (The spiral was maintained at bright yellow during the combustion.) The burette and combustion tube were connected, and the control stopcock of the burette opened to the constriction with the mercury reservoir connected thereto placed above the top of the burette. In this manner the gas was passed very slowly from the burette into the combustion pipette. The first passage usually required between 15 and 20 minutes. This insured the continued presence of excess oxygen around the combustion spiral, and prevented thermal decomposition of the ethane (which occurs when the sample is passed into the combustion pipette at the rates normally specified in the literature). After the first prolonged passage, 4 additional passages were made at rates varying from 5 to 3 minutes. The residual gas was measured and the total contraction upon burning was thus determined.

At this point the procedure took one of two courses, depending upon the method used for determining the carbon dioxide produced by the combustion.

When the regular method was employed, the procedure was as follows: Gas contained in the arm of the manometer connected to the compensator was taken into the burette, whence it was passed, together with the residue from combustion, into the pipette containing potassium hydroxide solution. The measured portion of nitrogen was transferred from storage in the "pyro pipette" to the burette and thence to the "KOH pipette." After returning the combined gases from the KOH pipette, 2 more passages into this pipette were made, followed by 1 passage into the combustion pipette (to regain carbon dioxide from that section of the distributor), and finally 2 passages into the KOH pipette. The residual gas was measured, establishing the amount of carbon dioxide formed during the combustion. Gas from the manometer was again taken into the burette and, together with the residue remaining after the absorption of carbon dioxide, was passed three times into the pyro pipette, once into the KOH pipette, once into the combustion pipette (thus regaining oxygen from these parts of the distributor), and finally twice into the pyro pipette. The residue from this absorption was measured and the excess oxygen determined. The oxygen consumed during the combustion was thus determined, as was the nitrogen (if any) in the original sample.

When the carbon dioxide was determined by absorption on ascarite, the procedure following the combustion was altered. After displacing the gas from the manometer, the residue from the combustion was passed slowly through the ascarite U-tube into the combustion pipette. The stored nitrogen was added as before, and the combined gases passed directly from the combustion pipette to the burette, by-passing the ascarite tube. This method of routing the gases was followed regularly. Repeating this procedure five times was sufficient to flush all of the carbon dioxide from the distributor connections and collect it in the ascarite. Completeness of absorption was determined by repeating the procedure. After thus determining the carbon dioxide produced during the combustion, the excess oxygen was obtained by 4 passages through the ascarite tube to the pyro pipette, 1 (with ascarite by-passed) to the combustion pipette, and 2 final

passages to the pyro pipette. Completeness of absorption was determined as before. All gas volumes were measured with the ascarite tube connected as part of the distributor when the pressure was finally balanced.

The removal of carbon idoxide by a dry reagent was resorted to in order to eliminate, so far as possible, the errors arising from changes in the amounts of gases dissolved in the potassium hydroxide solution. The alkaline pyrogallol solution is in contact with nitrogen alone after the absorption of oxygen, and the chances of error caused by a change in the amount of nitrogen dissolved are not so great as may be encountered with the potassium hydroxide solution. This solution is in contact with mixtures of oxygen and nitrogen of varying composition, and it is not impossible to lose or gain small but sometimes significant amounts of oxygen during the absorption of carbon dioxide. Furthermore, since it is necessary to pass the gas after the absorption of oxygen into the KOH pipette in order to regain oxygen kept in this part of the distributor after the absorption of carbon dioxide, the danger of displacing oxygen from the potassium-hydroxide solution and changing the volume of excess oxygen is not negligible, since nitrogen may also be exchanged in this process.

The first five of the determinations reported were made using the wet reagent for the removal of carbon dioxide, while the dry reagent was used for the rest. The differences obtained between the two procedures are small and will not be discussed further in the present paper. A later report will deal with this type of error, as it may occur in usual practice.

IV. ANALYTICAL RESULTS

The data obtained will be represented as follows: S, volume of the sample; TC, contraction after burning ("total contraction"); CO_2, volume of carbon dioxide produced; O_2, volume of oxygen consumed; N_2, volume of nitrogen in sample (if any). The same symbols will be used to identify numbers representing relative volumes in a volumetric equation.

If the reaction

$$C_2H_6 + 3.5\ O_2 = 2CO_2 + 3H_2O$$

is complete and the only reaction which takes place, if the gases measured were all ideal gases, and if there were no errors of manipulation or observation and no gains or losses through solution or otherwise except during the absorption of a constituent in the reagent intended for it, the volumes observed would correspond exactly to following equation:

$$C_2H_6 + 3.5\ O_2 = 2CO_2 + 2.5\ TC. \qquad (1)$$
$$1\ \text{vol.}\quad 3.5\ \text{vol.}\quad 2\ \text{vol.}\quad 2.5\ \text{vol.}$$

The observed volumes did not correspond exactly to this simple equation, and the remainder of this paper will be devoted to a discussion of some of the probable reasons why they did not correspond, and of the results of assuming that they did. The last assumption is, of course, the one usually made in reporting analyses.

The results of 18 analyses of the pure ethane are shown in table 2. The observed values of each of the three important quantities $\frac{TC}{S}$, $\frac{CO_2}{S}$, and $\frac{O_2}{S}$ were plotted, and a selection made of what appeared to be the best average value, which was slightly different from the arithmetical average of all observations, since in each case a small number of extreme values appeared to be the result of accident or inaccurate observation. An equation in which these averages are used,

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC, \quad (2)$$

is believed to represent, as well as any that could be chosen from the observed data, the deviations from the ideal conditions (represented by equation 1) which are inherent in the process and not the result of random error.

TABLE 2.—*Observed results of 18 determinations of ethane*

[For an explanation of the symbols used consult the text, p. 789]

Analysis no.	$\frac{(TC)}{S}$	$\frac{(CO_2)}{S}$	$\frac{(O_2)}{S}$	Carbon dioxide in products of combustion	N_2 (ml.)
				Percent	
1	2.5201	1.9846	3.5080	74.1	+.07
2	2.5168	1.9959	3.5120	76.5	−.01
3	2.5207	1.9965	3.5148	67.1	−.05
4	2.5200	1.9968	3.5145	66.1	−.05
5	2.5117	1.9918	3.5015	70.9	−.04
6	2.5191	1.9944	3.5041	64.9	−.18
7	2.5179	1.9930	3.5103	67.5	−.01
8	2.5169	1.9903	3.5033	69.5	−.08
9	2.5238	1.9937	3.5133	67.8	−.03
10	2.5109	1.9904	3.5014	71.3	.00
11	2.5156	1.9911	3.5179	78.8	+.12
12	2.5242	1.9949	3.5106	86.9	−.06
13	2.5204	1.9950	3.5149	71.4	−.01
14	2.5171	1.9990	3.5132	63.9	−.06
15	2.5203	1.9995	3.5170	72.4	+.03
16	2.5205	1.9915	3.5158	68.3	−.10
17	2.5223	1.9962	3.5139	66.2	−.01
18	2.5228	1.9972	3.5197	67.8	
Arithmetical average	2.5190	1.9940	3.5116	70.6	−.03
Selected average	2.520	1.994	3.513		
Probable systematic error	±0.003	±0.003	±0.003		

If ethane is known to be the only combustible compound present, the amount can be computed from the oxygen burned, the carbon dioxide formed, or the contraction, or from various combinations of these quantities. Most gas analyses are computed on the assumption that the ideal volumetric relationships will prevail as represented by equation 1. If this assumption were correct, all the methods of calculation would give identical results whatever the purity of the sample, and with ethane of the purity of that used, the common result should have been 100 percent.

TABLE 3.—*Results of computing ethane from average observed data by the use of various formulas*

[In each case the formula stated multiplied by 100 gives the percentage of ethane]

No.	Formula	Ethane found
		Percent
1	$TC/2.5S$	100.80±0.12
2	$CO_2/2S$	99.70± .15
3	$O_2/3.5S$	100.37± .08
4	$(TC+CO_2)/4.5S$	100.31± .1
5	$(TC+CO_2-O_2)/S$	100.10± .3
6	$[CO_2/2S+(TC+CO_2)/4.5S]/2$	100.00± .15
7	$(CO_2/2S+O_2/3.5S)/2$	100.04± .2

The results of computing ethane by various formulas are shown in table 3. In each case the selected average of the observed values for $\frac{TC}{S}$, $\frac{CO_2}{S}$, and $\frac{O_2}{S}$ given at the bottom of table 1 was used to compute the most probable result.

The indicated uncertainty in the result was estimated, as before, by plotting the percentages of ethane computed from each of the 18 analyses and disregarding a few extreme results believed to be certainly the result of random errors.

By the use of the first three formulas the percentage of ethane is, of course, simply computed from the three quantities which are independently observed during the analysis. Formula 4 has the merit of eliminating the effect of any error in the measurement of the products of combustion before the absorption of carbon dioxide, of deviations of carbon dioxide from the simple gas laws and of any loss, by solubility or otherwise, of carbon dioxide before the final absorption. This is true because any error in this part of the analysis affects the total contraction and the carbon dioxide to equal and opposite extents. Formula 5 has the merit of simplicity of computation and in this case appears to give a good result. However, the effect of any loss of oxygen during the course of the analysis (by oxidation of metals or previously deposited carbon in the pipette, or solution in the distributor or in the reagent for carbon dioxide, etc.) is seven times as great as when the ethane is computed from formula 3. This probably accounts for the relatively great scattering of results computed with this formula. Because formula 2 gives results that are consistently too low and formula 4 results that are consistently too high by almost exactly the same amount, the temptation to average the results of the two (formula 6) could not be resisted. The same fortuitous relationship exists between formulas 2 and 3 (formula 7).

When it is not known that ethane is the only hydrocarbon present, the amounts of two hydrocarbons, ethane and methane or ethane and propane, can be computed from any two of the three quantities which are independently observed in the analysis, or from one of these quantities and a combination of the other two. Again, ideal reactions, obedience to the simple gas laws, and correct observation would result in exact agreement among the results of analysis computed by different methods, whatever the hydrocarbons present; and in the case of the pure ethane, the amount of ethane found would be 100 percent. In table 4 are the results of computing ethane and methane

or ethane and propane from each of the three possible pairs of observed quantities and from the oxygen consumed and the sum of carbon dioxide and total contraction. The latter method (formula 11) possesses the merits mentioned in connection with the computation of ethane alone from the sum of the carbon dioxide and the total contraction, and is the only combination of the three observed quantities which seems worth using in computation. The combination used in normal practice (9) is apparently worthless.

A negative percentage of methane, computed from any formula, indicates an equal positive percentage of propane; the analysis should then be recomputed in terms of ethane and propane. If a negative quantity of propane is indicated, the situation is, of course, reversed. Computation from the average values for any pair of the observed quantities indicates the presence of methane; computation from the fourth formula (11) indicates the presence of propane rather than methane.

TABLE 4.—*Results of computing ethane and methane or ethane and propane from average observed data by the use of various formulas*

[In each case the formula stated, multiplied by 100 gives the percentage of the hydrocarbon]

No.	Constituent	Formula	Hydrocarbons found			
			C_2H_6	CH_4	C_3H_8	Total
			Percent	*Percent*	*Percent*	*Percent*
8	Ethane	$(4CO_2-2O_2)/8$	95.0			
	Methane	$(4O_2-7CO_2)/8$		9.4		104.4
9	Ethane	$(4CO_2-2TC)/3S$	97.9			
	Methane	$(4TC-5CO_2)/3S$		3.7		101.6
10	Ethane	$(O_2-TC)/S$	99.3			
	Methane	$(7TC-5O_2)/4S$		1.9		101.2
11	Ethane	$[10(TC+CO_2)-12O_2]/3S$	99.8			
	Propane	$[9O_2-7(TC+CO_2)]/3S$			0.3	100.1

The wide divergence from correct values of the results of computations in which the amount of carbon dioxide produced by combustion is involved seems to indicate that this introduces too great a total error. Its elimination by means of formula 11 appears desirable if analyses are to be computed without correction for deviations from the simple gas laws or other conditions which may be known to affect the result. This formula possesses the merit of relieving the chagrin of the analyst who obtains such total percentages as 101 to 104.

V. PROBABLE SOURCES OF ERROR

No attempt will be made here to make a complete list of all the possible sources of error attending the usual volumetric gas analysis. However, the deviations of the observed data from those which would be necessary to correspond to the ideal equation (1) are too large and too systematic to be attributed entirely to accidental or random errors. They must have resulted in part, at least, from conditions which recur in every analysis. Some of the more probable and important of these will now be discussed.

1. ERRORS CAUSED BY THE DEVIATIONS OF ETHANE AND CARBON DIOXIDE FROM IDEALITY

First in apparent importance is the fact that ethane is not an ideal gas but that a given weight (or given number of moles) of it occupies less space than corresponds to Avogadro's law. Unfortunately, completely reliable data for estimating this deviation are lacking, but from the best information available it appears that a given quantity of ethane will occupy, at atmospheric pressure and average laboratory temperature, only 0.990 of the volume computed from its molecular weight and the assumption that it is an ideal gas.

We must next consider that carbon dioxide is not a perfect gas. At atmospheric pressure and laboratory temperature the volume of carbon dioxide is about 0.994 of that of an ideal gas. If the pressure is lowered, the deviation from the ideal becomes less and approaches zero as the pressure approaches zero. The problem is complicated by the fact that the molecular volume is without doubt affected by other substances present. However, this effect is probably so small that it will be within the limit of possible accuracy of the analysis to assume the deviation of carbon dioxide from its theoretical molecular volume to be proportional to its partial pressure in a mixture. The percentage of carbon dioxide in the mixtures in which it was measured during the analyses averaged 70. Making the correction corresponding to the assumption stated, and also the correction for the deviation of ethane, the volumetric relationship, instead of being represented by equation 2, should be represented by the equation

$$0.990\ C_2H_6+3.5\ O_2=2\ (0.9958)\ CO_2+2.498\ TC \qquad (3)$$

which reduces to

$$C_2H_6+3.535\ O_2=2.012\ CO_2+2.523\ TC \qquad (4)$$

This does not correspond to the observed facts.

This disagreement with the observed facts is worth a moment's reflection on the part of the gas analyst. The reason for this is that, while most gas analyses are computed from the ideal volumetric equations, the present tendency to correct such results (if any correction is made) is based upon the assumption that the only existing error is that caused by the deviations of the imperfect gases from their theoretical molecular volumes. Since this more dignified effort has been accepted as an entirely sufficient corrective, it appears worth while to make a direct comparison of the results obtained from the ideal equations with those obtained from the same equations corrected for deviations of ethane and carbon dioxide from ideality. Such a comparison is made in table 5. It will be seen that corrections for the deviations of these gases do not remedy the situation, and in some cases the corrected equation leads to even greater errors than are obtained from the uncorrected equation. It is obvious that other errors, such as those discussed in the following section, must be considered.

TABLE 5.—*Comparison of the results obtained from formulas derived from the ideal volumetric equations with those obtained from the same formulas corrected for the deviations of ethane and carbon dioxide from their theoretical molecular volumes*

Formula (multiply by 100 to obtain percentages)	Percentages obtained from the ideal gas equations (arithmetical average of 18 analyses)		Percentages obtained from the ideal gas equations corrected for the deviations of C_2H_6 and CO_2 from their theoretical molecular volumes	
	C_2H_6	CH_4	C_2H_6	CH_4
TC/2.5S	100.76		99.81	
CO_2/2S	99.70		99.13	
O_2/3.5S	100.33		99.32	
(4TC−5CO_2)/3S	97.93		98.00	
(4CO_2−2TC)/3S		3.55		2.28

2. ERRORS CAUSED BY LOSSES OF ETHANE AND CARBON DIOXIDE DURING THE ANALYSIS

Next, consider the loss of carbon dioxide which occurs during a combustion. This may happen in 3 ways, and as a consequence may make the observed CO_2 too low and TC too high by a corresponding amount. The 3 avenues offered for escape of carbon dioxide are:

(1) Solution in the water formed during combustion. This water is condensed in the presence of the carbon dioxide formed during combustion and will, hence, be saturated. At the laboratory temperatures observed during these analyses, water will dissolve about 0.8 of its own volume of pure carbon dioxide. Since the effect is proportional to the concentration of the carbon dioxide (0.70 in this case), and since the average amount of water produced by a single combustion was about 0.05 ml, the amount of carbon dioxide lost should be approximately 0.04 ml.

(2) Solution in the other water present in the apparatus. This includes both the water present in the burette and the condensate from previous combustions which collects in the combustion pipette. The latter is not allowed to accumulate beyond a volume of about 0.2 ml. Furthermore, it may be assumed to be in substantial equilibrium with carbon dioxide. On the other hand, the water on the burette walls is taken fresh at the start of each analysis. It is present as a film or in small droplets. The total amount present is small but varies somewhat with the condition of the burette wall. There is never enough present to obscure the mercury meniscus, although there may be as much as 0.05 ml on the glass wall, as determined by actual observation. Just how much carbon dioxide will be dissolved is not known, nor could any fixed correction be derived. However, the correction would be small and the actual variation would not be great.

(3) Solution in the rubber connections of the distributor or manifold. There are 3 of these involved, 2 of which the carbon dioxide must pass on its way back from the combustion pipette. These connections are formed by butting together glass capillaries which are ground flat at the ends in order to present a minimum of surface to the rubber

tubing, and the rubber sleeve itself is secured at both sides by several turns of waxed dental floss. Blank analyses established the fact that approximately 0.05 ml of pure carbon dioxide was lost in the distributor of the apparatus during the average time of contact for a combustion. If the loss is proportional to the average concentration of carbon dioxide in the products of combustion, about 0.04 ml could be accounted for.

The order of magnitude of the error representing the entire loss of carbon dioxide during combustion should, therefore, be at least 0.08 ml.

Equation (4) corrected for this loss becomes

$$C_2H_6+3.535\ O_2=2.008\ CO_2+2.527\ TC \qquad (5)$$

A similar correction should be made for the observed solubility of ethane in the stopcock lubricant and rubber connections. The pure sample is in contact with 2 of the rubber connections previously described for about 20 minutes during its passage to the combustion pipette. Blank analyses established the order of magnitude of the loss of ethane as about 0.06 ml. The loss of ethane, propane and butane were measured in the distributor of the apparatus and also in a rubber tubing of 10 cm length. In the case of butane, the loss was considerable in the distributor and furthermore it was possible to regain some dissolved butane by passing another gas, e.g., nitrogen, through the distributor. Ethane should behave in a smilar manner, so that it would be possible to lose a small portion of the sample at the beginning of the analysis and regain an indeterminate amount later on. This behavior makes a blank correction difficult, even if all other circumstances were identical for each analysis. The fresh nitrogen balance obtained for each analysis would prevent the ethane from reaching any saturation equilibrium in the distributor, and no constant error could be expected from this source, although it might be a constantly present one.

This makes a definite correction for ethane somewhat uncertain, although the need of one is clearly indicated.

On comparing equation (5) with equation (2) it is apparent that the "corrected" values for oxygen consumed, carbon dioxide produced and total contraction are all too high to agree with the observed results. If some ethane was lost by solution or otherwise before combustion, the corrected equation can be brought into better agreement with the observed results. The deficiency of ethane to be accounted for is greater than the amount lost during blank analyses. However, if the latter loss is assumed to be substantially correct, and equation 5 is corrected accordingly, the equation.

$$C_2H_6+3.525\ O_2=2.002\ CO_2+2.520\ TC \qquad (6)$$

is obtained.

If the rather uncertain correction for the deviation of ethane from Avogadro's law as too great, the "corrected" results might be brought into good agreement with those actually observed. It is interesting to assume this, if merely for the sake of ascertaining how far the original value of 0.990 assumed for the deviation of ethane would have to be altered. If such arithmetical thaumaturgy is in-

voked to the extent of transforming the ethane correction to 0.993, equation (6) becomes

$$C_2H_6+3.515\ O_2=1.995\ CO_2+2.516\ TC, \quad (7)$$

which represents the observed data,

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC, \quad (2)$$

in most respects.

3. ERROR IN THE RESIDUAL NITROGEN

At the end of each analysis the residual nitrogen was measured. Usually it did not have exactly the volume taken at the start to fill the distributor and the upper part of the compensator. In the 18 analyses the differences represented an average loss of 0.03 ml, but these differences were erratic, except for the fact that a loss was observed in 13 out of 18 cases. However, 0.03 ml is within the probable error. It was thought possible that the loss of nitrogen was caused by oxidation, but a test of the water, produced during several combustions, by the standard method employed in water analysis showed no trace of nitrates.[5] A number of blank tests were made by passing over the hot wire both air and mixtures of oxygen with the approximate amount of nitrogen present in the manometer and distributor. Small contractions were observed, but no assurance was obtained that an error of definite magnitude had been discovered.

Further evidence tending to support the belief that no loss of nitrogen occurred by oxidation was obtained as follows. Approximately 28 liters of air was passed over a heated platinum spiral and the exit gas was passed through a solution of potassium hydroxide. The rate of passage was approximately 20 ml per minute and the temperature of the wire closely duplicated that of the analyses. The platinum spiral was three times the length of the one used in the analyses, and was suspended in a tube of 5-mm bore so that intimate contact with the air stream was insured. The potassium hydroxide solution was examined for nitrates or nitrites, by reducing with Devarda's metal and testing for ammonia with Nessler's reagent. The test indicated that the amount of nitrogen lost could not have been as great as 0.001 ml per 100 ml of air.

In view of these facts, no correction was attempted. The possibility of a small error of this nature still remains, however, since the oxidation of nitrogen may have occurred during the actual combustion of ethane to a greater extent than indicated by tests with air.

VI. CONCLUSION

In having thus indicated probable sources of error that account for most of the discrepancy between the ideal equation and the average of the observed results, it must not be assumed that the corrections offered are necessarily always of the right magnitude or that other sources of error do not exist. The purpose of this paper will be accomplished if attention is generally directed to three facts: (1) that analyses of hydrocarbons computed from the ideal equation

[5] Notes on Practical Water Analysis, by W. D. Collins, U.S. Geol. Survey Water Supply Paper no. 596-H, 241, 1928. The analyses were made by E. Wichers and F. W. Schwab of the Bureau of Standards.

should not be regarded as necessarily accurate, no matter how carefully the work is done; (2) that corrections for deviations from ideality of the imperfect gases are not always sufficient to eliminate the inaccuracy; and (3) that there are numerous minor sources of error for which it may or may not be possible to make satisfactory corrections.

While the sources of error which have been considered do not afford the complete or, necessarily, the entirely correct explanation of the facts observed, the facts themselves do offer an empirical solution to the problem of computing the analysis of ethane. As far as the present work is concerned, formulas derived from the observed volumetric equation (2)

$$C_2H_6+3.513\ O_2=1.994\ CO_2+2.520\ TC$$

would give considerably more accurate results than could be obtained from the established formulas in general use. It is interesting to consider the probable extent to which the general application of this equation is justified.

From a study of the nature of some of the errors which are known to have been present, it is apparent that the actual values observed depend primarily upon three general factors: 1, the gas examined; 2, the technique employed, and 3, the particular apparatus used. It is obvious that equation (2) cannot be generally useful unless the conditions at hand closely approximate those existing in the present work. First, the general application is at once limited to the analysis of ethane, or mixtures containing very high percentages of ethane and no other combustible gas. Second, a variation of the technique employed might greatly influence the values obtained. However, the one prescribed in this report can be reproduced, perhaps advantageously in some cases. If this is done, equation (2) may retain its general usefulness. Third, the errors caused by losses of ethane and carbon dioxide must be substantially duplicated in any apparatus. It cannot be supposed that this condition will ever be entirely realized. The extent to which these errors will be reproduced in different apparatus is uncertain. However, apparatus of this general type usually include the same number of rubber connections and stopcocks, and it is not unlikely that a fairly average condition was represented in the present work. If this is substantially true, equation (2) may still be considered as fairly suitable for general use. It is at least not inconsistent to suppose that its use would improve the accuracy of such analyses. The safer procedure, of course, would be for the analyst to calibrate his own apparatus and technique by means of a sample of ethane of known purity.

It is proposed to continue the development of empirical volumetric equations of this type for other gases, both pure and in known mixtures, in the effort to improve the accuracy of the slow combustion method.

While it may be possible to substantially improve the accuracy of this method, the data obtained for ethane indicate that highly accurate results cannot be obtained by the usual volumetric procedure. This suggests recourse to gravimetric combusion methods for those cases in which the accuracy demanded may justify a relatively complicated and time consuming procedure.

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EFFECT OF HEAT TREATMENT ON THE EXPANSIVITY OF A PYREX GLASS

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ABSTRACT

Heating a pyrex glass at different temperatures between 450° and 750° C. caused its mean linear expansivity between 20° and 200° C. to change more than 10 percent. This expansivity in the case of the original untreated specimen was approximately 0.0341×10^{-4} and after treatment at temperatures near 750° C. it increased to 0.0345×10^{-4}, while treatments at 450° C. reduced it to 0.0307×10^{-4}. After any such changes the original expansivity could be restored by a heat treatment near 650° C. Treatments between 650° and 450° C. appeared to reduce the expansivity rather steadily as the treating temperature was lowered.

These results indicate that there is some advantage in annealing this glass at the lowest practical annealing temperature since any reduction in the expansivity should increase the resistance of the glass to heat shock.

In a previous paper[1] it was pointed out that in some cases the heat treating of glass in the annealing range noticeably affects the magnitude of the expansivity. In addition to this, very little is known concerning such expansivity changes except that they are seldom large. Without more definite data regarding their actual magnitude it would also seem possible, however, that under certain conditions they may have an appreciable effect on the serviceability of glass. Moreover, unless their magnitude is better known it may be suspected that these changes are a controlling factor in producing the dimensional changes which are usually very easy to detect if the dimensions of the glass sample are measured under standard conditions both before and after it receives heat treatment in the annealing range.

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I. INTRODUCTION

From the standpoint of what may be attained in the way of dimensional changes under the usual conditions of production, it is ordinarily not feasible to alter the density of most glasses more than 2 or 3 percent by varying the heat treatment; and in view of this it may be thought that any changes which can be produced in the expansivity by the same cause and under the same conditions would never greatly exceed such a limit. In the production of most glassware an expansivity change no greater than this would generally be considered as relatively unimportant. Practical considerations soon show, however, that definite data on this effect of heat treatment are required because of the possibility that the changes in the expansivity may

[1] Tool, Lloyd, and Merritt, J. Am. Ceramic Soc., vol. 13, p. 653, 1930.

materially exceed 3 percent for some glasses and also because even smaller changes can under certain special conditions assume a real importance. For example, relatively small changes of this sort, if they are not uniform throughout a piece of ware, may cause a differential expansion that can easily be detrimental whenever such ware is heated or cooled. Especially in articles designed for precision measurements, nonuniformities of this character may often be the source of very troublesome distortions; and such distortion may occur even when the differential expansions developed during normal temperature changes are so small that the accompanying stresses fall very far below the breaking limit. Presumably such conditions of nonuniformity are more likely to appear in a ware consisting of several parts fused together, although they may also be present in any article fabricated under conditions which preclude a thoroughly uniform and sufficient annealing treatment.

If certain glasses are found for which the relative changes produced in the expansivity by heat treatment are comparatively large, it is always possible that in some of these cases it may be quite advantageous to control the expansivity by modifying the heat treatment. This would be especially true if the glasses in question are of types which are valuable because of their low expansivity. That the expansivity changes obtainable by heat treatment may in some cases materially exceed 3 percent was shown by some preliminary work in which it was found that heat treating a sample of pyrex tubing at 550° C., which is not an extreme annealing temperature, reduced the expansivity 6 percent or more.[2] Presumably the tubing had originally been cooled quite rapidly to room temperature after being made; and in that case it doubtless had a relatively high effective treating temperature. This consideration, together with the above result, would make it appear that lowering the annealing temperature of this type of pyrex glass reduces the expansivity materially.

In at least a portion of the annealing range, lowering of the annealing temperature also appears to reduce the specific volume, V_t, at 20° C; and, since the expansivity is apparently decreased coincidently, it follows that the corresponding volume change, ΔV_a, during the annealing is a greater decrease than the ΔV_t and that the difference between these decrements is greater than that which would be caused by an unchanged expansivity.[3] It is, however, difficult if

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[2] Dimensional Changes Caused in Pyrex Glass by Heat Treatment, informally reported at the 1930 meeting of the American Ceramic Society, Toronto, Canada. The composition of this glass and also that on which the following expansivities were obtained is SiO_2 80.7, R_2O_3 2.1, Na_2O 4.0, and B_2O_3 (by difference) 13.2 percent.

[3] That is, if the original volume of any glass sample at a given temperature, T_t, is V_t, and after being heated rapidly to T_a (a chosen treating temperature in the annealing range) immediately becomes V_a, then these volumes may be related by the usual expression, $V_a = V_t[1+\beta(T_a - T_t)]$, where β is the average volume expansivity and has a value determined by the temperature interval, $T_a - T_t$, and the condition of the glass. During continued heating at T_a the volume V_a will in time change to a constant value V_a', and β to β', so that when the sample is ultimately cooled rapidly to T_t a volume V_t' is obtained and

$$V_a' = V_t'[1+\beta'(T_a - T_t)]$$

From this it follows that—

$$\Delta V_a = \Delta V_t + [\Delta\beta . V_t + \beta . \Delta V_t](T_a - T_t),$$

where $\Delta V_a = V_a - V_a'$, etc. If both V_t and β are decreased after a heat treatment it is evident that these decreases will both contribute in the same sense to a computed value for the change in V_a. The above equation may also be written in the form

$$\Delta V_a - \Delta V_t = \Delta V_t \beta (T_a - T_t)\left(\frac{\Delta\beta}{\beta}\frac{V_t}{\Delta V_t} + 1\right)$$

which, assuming that β and $T_a - T_t$ are approximately 3×10^{-5} and 500° respectively for ordinary glasses, makes it obvious that $\frac{\Delta\beta}{\beta}$ must be about nine or ten times as large as $\frac{\Delta V_t}{V_t}$ if $\Delta V_a - \Delta V_t$ is to approximate 15 percent of ΔV_t.

It should be noted that in developing such relations as the above it may be necessary, in some cases, to include terms containing the square and possibly higher powers of the temperature, especially if the temperature interval considered is large.

not impossible to measure ΔV_a with an accuracy which would demonstrate this.

If in other portions of the annealing range of this pyrex glass a lowering of the effective treating temperature increases V_s as seems to be the case from previous studies,[4] it follows that a coincident reduction in the expansivity would signify a ΔV_a that is smaller algebraically than ΔV_s and possibly one that indicates a reduction of V_a as before. Ordinarily, however, the effect of a change in the expansivity is too small to produce this possible difference in direction between ΔV_s and ΔV_a. Moreover, observations on the dimensional changes during the process of annealing pyrex glass will usually show that both changes are ultimately in the same direction although the change in V_s may be observed to reverse its trend during the annealing period.[5] As a matter of fact, this reversal in trend suggests the possibility that at least two processes opposed in their volume effects are developed in this glass by annealing treatments which lower the effective treating temperature, and that the one which increases V_s proceeds at a relatively low rate. It is also believed that this possibility will, under certain assumptions, partially explain the minimum densities obtained[6] by treatments at temperatures near 550° C. more satisfactorily than any probable change in the expansivity. Before any reliable conclusions could be formed concerning this possibility it seemed necessary that the range of expansivity changes caused by treatments at different annealing temperatures should be studied more thoroughly.

II. SPECIMENS TESTED AND APPARATUS USED

The specimens tested were pyrex tubes of the kind ordinarily used in constructing chemical apparatus and had approximately a 12 mm outside diameter and a 1.5 mm wall. Ring sections approximately 5 mm in length were cut from these specimens and ground so that on each end of a section there were three short equally spaced legs with small feet. Before testing such samples, the slightly rounded bearing surfaces of the feet were polished reasonably smooth and so adjusted that the section when acting as a spacer between two flat interferometer plates of pyrex glass[7] would cause interference fringes of a suitable width to appear when this interferometer system was illuminated in the usual way with monochromatic light (e.g., helium, $\lambda = 5875.6$ A).

During an expansivity test this interferometer system rested directly on an interferometric thermometer plate of fused quartz in such a way that the fringes formed by this plate as well as those from the interferometer itself could be viewed simultaneously by a previously described[8] viewing apparatus. This complete system rested in a heavy

[4] Tool and Hill, J. Soc. Glass Techn., vol. 9, p. 185, 1925.

[5] Linear expansion curves showing this reversal in trend were exhibited in the above mentioned informal report.

[6] Tool and Hill, J. Soc. Glass Techn., vol. 9, p. 185, 1925.

[7] It has been found advisable, whenever possible, to use interferometer plates of the same glass as the test specimen. This prevents to a great extent differential expansion and almost eliminates the slippage between the plates and specimen which so often disturbs the equilibrium of the system and causes small but definite breaks and changes in slope in the expansion curves. Such disturbances are particularly apt to occur somewhat above 200 °C. where it appears that the lubricating gas films undergo a considerable change. Pyrex plates can be used to temperatures somewhat above 600° C., and those of other glasses to temperatures having corresponding positions in the appropriate annealing ranges.

The ring type of specimens used in these tests also adds greatly to the stability of the interferometer system. In some cases still greater stability has been obtained by fusing the spacer and plates into a single unit.

[8] Tool, Lloyd, and Merritt, J. Am. Ceramic Soc., vol. 13, p. 653, 1930.

aluminum cup which was covered by an aluminum lid containing a small, fused-quartz window. During the observations the cup and the contents were heated and cooled in an upright tubular electric furnace at a rate of about 3° C. per minute. The cooling rate of the furnace could be regulated by forcing air through a chamber which inclosed the heating elements.

III. HEAT TREATMENTS OF SAMPLES

Before the final adjustment of the test samples they were divided into lots and each lot was then treated at one of the several chosen treating temperatures spaced at intervals of 25° from 450° to 750° C. A horizontal tubular electric furnace whose temperature could be controlled over a considerable time to within ±5° C. was employed for such treatments. The periods of treatment employed at these temperatures were based on experience gained during an investigation of the time required to obtain a density equilibrium for this glass at various treating temperatures. (See footnote 4 for reference.) Such periods ranged from 2 months at 450° to 30 minutes at 750° C. At 450° C. a period of 2 months is possibly too short to produce the maximum effect, but it is estimated that it causes in excess of nine tenths of the total change possible.[9] An appreciably closer approach requires an unduly long treatment. At 750° C. a period of one half hour may also be somewhat insufficient. The possibility of devitrification, which occasionally becomes noticeable after several hours' treatment somewhat above 650° C. makes it necessary, however, to reduce the periods as much as possible in this range. The periods at all the higher temperatures were therefore made as short as seemed consistent with a reasonable approach to a stable density while the glass still remained in the undevitrified[10] state. After treating the glass for the periods mentioned, it was cooled rapidly in air; and, from temperatures above 550° C., the samples were shaken about on burned asbestos board for the first moments of the cooling. This agitation should make the cooling more uniform and somewhat more rapid. The resultant shortening of the cooling period is especially desirable since there is no doubt that some annealing, which may affect the various possible processes differently, occurs during the time required in cooling to 550° from temperatures above 600° C. Cooling at these rates from such temperatures naturally introduces a certain degree of strain and possibly some resultant inconsistency in the observed expansion data, but this cannot be avoided if the effects produced on the expansivity by high temperature treatments are to be preserved for tests at lower temperatures.

IV. METHODS OF OBSERVATION

As each interference (air) fringe, indicating a change of ½ λ or 293.78 μ in the height of the pyrex separator, passed the reference point of the interferometer system they were counted and recorded

[9] There were some indications in the previous work on density that very long treatments tended to yield values slightly lower than those reached after shorter ones. Such a result would correspond to the previously mentioned reversals which can be observed directly during a few hours' treatment at higher temperatures.

[10] It was necessary to avoid if possible the least trace of devitrification since that change in the glass greatly increases the observed expansion and consequently the apparent expansivity for the range from 100° to 200° C and at the same time makes a determination of the true expansivity impossible. For a discussion of the terms "true" and "apparent" expansivity see Tool and Eichlin, B.S. Jour. Research, vol. 6, p. 523, 1931.

along with the simultaneously determined number of fringes (including fractions) which had passed the reference point of the refraction thermometer and which indicated the corresponding change in temperature. For the approximate temperature range, 25° to 200° C., which was used in these tests the total change in the number of air fringes and thermometer fringes averaged about 9 and 27, respectively.

Each test consisted of two complete heating and cooling cycles and consequently furnished four determinations of the temperature (as indicated by the accumulated number of refraction thermometer fringes) for each air fringe. The average of these four temperature determinations and the relative change in length in microns per centimeter, $\frac{\Delta l}{L}$,[11] were used to determine the points for a tentative expansion curve. These points (approximately nine in number) fell on a practically straight line although a large-scale plot usually made noticeable a very slight convexity toward the temperature coordinate.

After a heating and a cooling cycle the measurements usually showed a slight "apparent shortening" of the samples especially in the case of those treated at the higher temperatures. This effect, if it is a real shortening or contraction, is doubtless in some degree similar to such annealing effects as slight deformations under stress and perhaps to very small specific volume changes similar to those found in the normal annealing range although not necessarily of the same sign. It was found, moreover, that these "shortening effects" were usually somewhat larger during the first cycle of heating and cooling; consequently, each sample was subjected to a preliminary cycle before the actual test began. This seemed especially advisable since a large part of the effect, during the first cycle at least, may well be considered as only an apparent contraction caused by an attenuation of the thin air films between the feet of the specimen and the interferometer plates rather than to the above-mentioned possibilities.

Since the tentative expansion curves were all very nearly straight lines and since only the average expansivities for the temperature range were desired, it seemed sufficient to make the assumption that $\left(\frac{\Delta l}{L}\right)_T = A + BT$, where B is the expansivity expressed in microns per cm per degree centigrade. To compute B as objectively as possible and, for comparative purposes, as carefully as repeated tests on a given sample appeared to warrant, it seemed desirable to discard the graphical procedure and to use the method of least squares. In the 15 cases where two or more tests were made on a sample, there was only one case in which the total difference between the computed values of B for a given sample was as great as 1 percent. The much larger spreads shown in the table of results arise from the use of more than one sample for the determinations at a given treating temperature.

V. RESULTS

The results for B presented in the table and figure are averages of two or more determinations on one or more samples as indicated. While the maximum spread of the results for a given treating tempera-

[11] The ratio, $\frac{\Delta l}{L}$, was determined from the length, L, of the sample at room temperature and from the increase in length, Δl, as computed from the number of air fringes and the wave length of the light. Corrections were employed which allowed for the temperature change in air refractivity.

ture is not in every case as small as might be desired, it is seldom excessive and never sufficient to indicate that the expansivity failed to increase as the treating temperature was increased if the range above 625° C. is excepted. For treatments in this range, however, relatively erratic results are to be expected as previously noted.

From the results obtained it was found that the linear expansivity, $\alpha\left(=\frac{\beta}{3}\right)$ increases from about 3.075×10^{-6} to 3.420×10^{-6} as the treating temperature is increased from 450 to 650° C. This is an increase in excess of 10 percent and agrees well with the tentative value of 6 percent (given in the informal progress report cited above) as the increase for a shorter range. This range probably did not exceed 100° since, as previously explained, it was limited by the treating temperature for that determination, 550° C., and the relatively high effective treating temperature of the original glass which probably did not exceed 650° C.

Some tests made on the original glass during the present investigations give 3.406×10^{-6} as the average result for its expansivity. This value would place the original effective annealing temperature of the glass above 625° C. In this temperature range, however, such results are not definitely indicative of the previous annealing treatment since no great change in the expansivity appears to be produced by treating the glass at temperatures from 625° to 750° C. unless incipient devitrification results because of the treatments. This failure of the expansivity to continue to increase with increasing treating temperatures may be interpreted as the result of an annealing [12] while the glass cools through the range above 600° C. However, definite proof of this possibility is lacking and is, moreover, difficult to obtain since the temperatures involved cause the glass to become appreciably deformable and subject to the introduction of strains.

After the expansivity has been reduced by a low temperature treatment it can be restored to its previous value by reheating at a higher temperature. This is demonstrated by the result (shown in the table) on a sample retreated at 675° C. after it had first been treated at 450° C. with the other samples yielding the results given for the latter temperature. The result on the last sample recorded in the table also shows this reversibility, although the value obtained for the expansivity is not as large as might have been expected for a retreatment

[12] The higher densities found by Tool and Hill for another specimen of pyrex glass after treatments from 600° C. up as compared to those found for treatments between 525° and 575° C. can to some extent be explained on the basis of the greater expansivities obtained at higher treating temperatures. Nevertheless, there is some indication that the minimum in the density curves may have resulted in part from the annealing received by the samples (which were treated at the higher temperatures) while they cooled through the range above 550° C. This effect of the annealing would be possible on the basis of the hypothetical processes mentioned in connection with footnote 5. That is, during cooling, the process causing contraction and occurring before the previously mentioned reversal, progresses much more rapidly and increases the density more than the opposed process acting simultaneously decreases it. This explanation assumes that this latter and slower process is only capable of showing its full relative effect when the annealing temperatures are low enough to prevent (in view of the rapid rate of cooling employed in the tests under consideration) the faster process from making any progress as the glass is cooled after a heat treatment.

The larger samples required for the density tests caused the possible rate of cooling to be lower than in the case of the very small rings used in the present investigation. It is probable, however, that even the more active process ceased to make any great progress soon after either type of sample reached 600° C. during the cooling involved in their preparation for test.

The composition of the glass used in these density tests is SiO_2 81.4, R_2O_3 2.2, Na_2O 4.0, and B_2O_3 (by difference) 12.4 percent. The differences in composition between this glass and that of the tubing previously mentioned are presumably incident to changes in the process of manufacture, since the above glass was produced several years earlier. The chemical analyses of these glasses were made by F. W. Glaze of this Bureau.

as high as 600° C. This low value is, however, accounted for by the fact that the sample which was first treated at 500° C. was retreated during an expansion test which extended to 600° C. and, as required by the test, cooled at the relatively slow rate of 3° per minute, which again reduced the expansivity somewhat.

Results of tests of this kind indicate the rapidity with which annealing and disannealing proceed. For example, one of the samples previously treated at 450° C. expanded, when subsequently disannealed by heating at a rate of 3° per minute and while passing through the 50° range just above 550° C., to an amount which was almost equal to the total normal expansion caused by the true expansivity alone in the range from 20° to 500° C. Moreover, the expansion developed so rapidly as 600° was approached that it could not by such a test be distinguished from a normal expansion. In fact, some of this expansion in the range between 550° and 600° C. is caused by the true expansivity of the material but it can be shown that at least 50 percent of it can ultimately be obtained by treating at 550° C. and without going to higher temperatures. Obtaining the expansion in this way shows that a large portion of it is a disannealing effect, although a much longer time is required because the physico-chemical changes involved in disannealing always progress at a greatly decreased rate at lower temperatures. For the same reason it is obvious that the annealing which occurs while cooling at the rate of 3° per minute from 600° C. to room temperature will not equal the disannealing caused by the previous heating to 600° C. at the same rate in such a test as the above; but, if the expansivity results mentioned in the previous paragraph are any criterion, such a cooling did reduce the effective annealing temperature from 600° C. (the upper limit of the test and the point where the sample was given ample opportunity to reach approximate equilibrium) to 550° C. The annealing effect caused by such a cooling is, therefore, about one half of the annealing effect obtained when a sample is thoroughly treated at 500° C., if such effects are measured in terms of effective treating temperature displacements.

VI. GENERAL DISCUSSION

Even from a practical standpoint small changes in the expansivity such as those found here have some significance in special cases. In glassware which is subjected to sudden temperature changes it is naturally desirable to reduce the expansivity as much as possible and in such cases these small reductions by treatment at relatively low annealing temperatures may be serviceable in reducing breakage from thermal shock. One point of special interest to be noted is that the increase in expansivity caused by treating at high temperatures will affect to some degree the gain in mechanical strength which may be obtained by so-called "tempering treatments." That is, a higher expansivity should assist somewhat in introducing the required strain to make the "tempered" ware more resistant to mechanical shock, but it may also increase the sensitivity of the ware to severe localized thermal shocks.

TABLE 1

Number of samples tested	Total number of tests	Treating temperature	Approximate treating time	Average expansivity B[a]	Greatest spread in results
		°C.	*Hours*	*Microns/cm.°C.*	*Percent*
2	3	450	1,610	0.0307	0.3
2	3	475	1,750	.0310	.4
2	3	500	1,030	.0313	1.0
2	3	525	720	.0317	.9
2	3	550	330	.0320	.4
1	3	575	170	.0326	.8
3	4	600	120	.0329	1.0
2	3	625	72	.0338	3.0
2	4	650	27	.0342	4.0
2	3	675	5.5	.0342	.7
2	3	700	3.0	.0341	2.0
2	4	725	2.0	.0345	3.0
2	3	750	.5	.0343	1.5
1	2	[b]		.0341	.8
1	1	[c] 450	1,610	.0342	
		[d] 675	6		
1	1	[c] 500	1,030	.0320	
		[d] 600	[e] 1		

[a] The values B when multiplied by 10^{-4} become the usual linear expansivities or coefficients of linear expansion designated by α in the previous pages.
[b] Untreated.
[c] First.
[d] Second.
[e] This treatment also included heating and cooling at a 3° C. per minute rate since it was given during an expansion test extending to 600° C. The samples in all other cases were cooled as rapidly as possible in air at room temperature.

From the more general viewpoint of gaining an understanding of the behavior of glass under the application of heat treatments such results as those shown in table 1 assume, however, a greater importance. The results on this particular glass show, for example, that the density when determined under standard conditions after various more or less complete heat treatments does not give an entirely adequate idea of the manner in which the density of the glass varies with temperature and time of treatment in the annealing range. They indicate also that the relatively rapid increases in size which are always evident in annealed samples, of this type of pyrex glass when subjected to expansion tests extending above 500° C. are probably caused to a small degree by an actual increase in the true thermal expansivity as the disannealing progresses. This increase is caused presumably by some of those same physico-chemical processes which produce the changes in volume which require time as well as a change in temperature within the annealing range for their accomplishment. Likewise it also appears probable that the well known slowing up of the rate of apparent expansion between 300° and 500° C. shown by expansion curves obtained by heating chilled samples is to some small extent the result of a decrease in the true expansivity as the annealing at lower temperatures progresses.

From the results depicted by the accompanying curves it is evident that the expansivity when determined with sufficient accuracy, possesses an advantage over density measurements as a means of determining the effective annealing temperature of a sample of this particular type of pyrex glass. This follows because it is apparent that in the range between 500° and 650° C. two treatments, one above 560° and the other below, may cause the glass to have the same density (or refractivity), whereas this is not true in the case of the

expansivity. Another advantage arising from the utilization of expansivity tests for this purpose is found in the possible use of much thinner and lighter samples which can be subjected to a more rapid cooling. In the case of this glass, the rapidity of cooling may be especially important if, as seems possible, there are two types of processes progressing at different rates during heat treatments in the annealing range and producing opposed changes in volume.[13]

In the beginning it was suspected that one of these processes was an adjustment antecedent to the process of devitrification and that it was probably the one which is slower and causes an increase in volume as the treating temperature is lowered. In that case it might also be suspected that its advancement would increase the expansivity in the range between 100° and 200° C. since the first product of devitrification so far detected after treatments at temperatures between

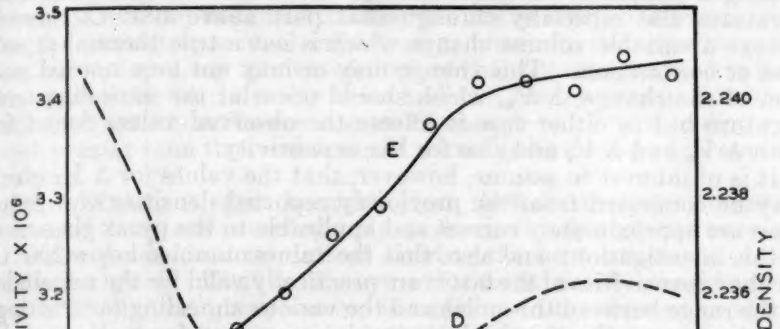

FIGURE 1.—*E. Graphic presentation of data shown in table 1. D. Reproduction of curve obtained by an investigation of the density changes caused by varying the annealing temperature*

[See references 2 and 4. The curve showing the refractivity changes is similar in form.]

625° and 750° C. is that form of cristobalite having an inversion near 200° C. In any event long treatments designed to advance the slower type of process as far as possible at the various treating temperatures show that something like devitrification is slightly active at points as low as 600° C.; and even slight traces of visible devitrification in samples so treated appear to cause a definite expansivity increase near the cristobalite inversion range. In the present investigation, however, the treatments employed at temperatures between 550° and 600° C. were sufficiently long to advance the volume increases, caused presumably by the slower process, to limits apparently unattainable above 600° C.; and yet the results show that these treatments reduced the expansivity steadily as the treating temperature was lowered. Moreover, no visible indications of devitrification appeared;

[13] See footnote 12, page 804.

consequently the existence of any direct relation between the volume-increasing process and that of devitrification seems doubtful.

Below 525° C. where the volume-decreasing processes are predominant it is also evident that the expansivity is reduced as the volume decrease is enhanced by lowering the treating temperature. This appears to indicate that these processes also are not directly related to devitrification, or at least not when they progress in this temperature range.

Any attempt to determine the idealized relation existing between the specific volume change, ΔV_s, which should be obtained at a standard temperature as the result of a heat treatment at some chosen annealing temperature and the corresponding change, ΔV_a, which should occur at the annealing temperature during treatment is practically impossible. This is the case because on heating or cooling a sample of the glass through the range between these temperatures and especially through that part above 300° C. there is always a variable volume change which is not a true thermal expansion or contraction. This change may or may not be a normal portion of the change, ΔV_a, which should occur at the annealing temperature but in either case it affects the observed values found for both ΔV_a and ΔV_s and also for the expansivity.

It is of interest to assume, however, that the values for ΔV_s which may be computed from the previously reported densities of a pyrex glass are approximately correct and applicable to the pyrex glass used in this investigation; and also, that the values obtained below 200° C. for the expansivities of the latter are practically valid for the remainder of the range between this point and the various annealing (or treating) temperatures. On this basis approximate values for ΔV_a may be computed. Thus, the densities at 20° C. for the previously investigated sample of pyrex glass were 2.2415 and 2.2330 after treatments at 450° and 550° C., respectively, while from the above table the expansivities obtained on the supposedly similar type of glass for the same treatments were 0.03074×10^{-4} and 0.03204×10^{-4}. A treatment at 550° after one at 450° C. will, therefore, produce the relative increases, $\frac{\Delta V_s}{V_s}=0.0038$ and $\frac{\Delta \beta}{\beta}=0.041$ in the specific volume and cubical expansivity. On assuming that the relation developed in footnote 3 is representative of the conditions involved, it follows that $\Delta V_a=1.06\ \Delta V_s$ approximately, whereas if the expansivity remained unchanged, the ratio $\frac{\Delta V_a}{\Delta V_s}$ would not greatly exceed 1.006 for treatments anywhere in the annealing range.

After a treatment at 550° C. another at 450° will not produce decreases equivalent to the above increases since it appears that the process is not entirely reversible [14] between these temperatures. Between 450° and 675° C., however, practically complete reversibility appears to exist. For treatments at these temperatures the densities obtained were 2.2415 and 2.2365, respectively, while the expansivities shown in the table are 0.03074×10^{-4} and 0.03423×10^{-4}. From these values [15] it follows that $\Delta V_a=1.33\ \Delta V_s$ which would indicate that

[14] Numerous ranges can be chosen where there is likely to be this lack of reversibility if the upper and lower limits respectively lie in the ranges 560° to 650° and 450° to 560° C. Moreover, ranges can be chosen where ΔV_s is practically zero and under such conditions ΔV_a becomes approximately $\Delta\beta.V_s(T_a-T_s)$.

[15] In these computations it has generally been assumed that T_a was the upper treating temperature. Obviously, using the lower temperature as T_a would alter the result somewhat.

in this case the relative magnitude of the two increments was appreciably affected by the expansivity change. Moreover, between 550° and 675° C., which is also a range of apparently complete reversibility, it will be found from the data given above that $\Delta V_a = 0.72 \Delta V_s$. In this case ΔV_a is the smaller change and both are decrements when the final treatment is at the higher temperature. To check this result by an experimental determination of ΔV_a is, however, especially difficult since at 675° C. the glass is somewhat deformable.

This comparatively large effect of the expansivity change in the two latter cases is due to the relative smallness of ΔV_s and ΔV_a for this range of treating temperatures, and in this connection attention must again be directed to the possibility that the negative increment in V_s for treating temperatures from 550° to 675° C. is to some degree the result of an annealing during the cooling from 675°. If this selective annealing effect between different processes actually exists, it should be reduced to some extent by the use of much smaller samples. For the present it seemed unnecessary, however, to investigate this possibility, expecially in view of the fact that the samples used in both the expansivity and density tests had the minimum size consistent with good results and were also small enough to allow a cooling rate much greater than that which would normally be employed in working the glass.

In conclusion it must be made clear that the expansivity results presented here are intended only as an indication of the range of variation possible as a result of altering the heat treatment of this particular glass. That is, these results must not be considered as typical of all pyrex glass, because in addition to the changes produced by heat treatment it is evident that differences in expansivity are caused by variations in composition between samples and possibly by other factors. Moreover, other possible combinations of heat treatments which may increase and complicate the expansivity changes have not been attempted in these tests. From the results presented it appears, however, that the points mentioned in the following summary have been established.

VII. SUMMARY

1. Lowering the annealing temperature in the range 650° to 450° C. reduced the mean expansivity of a pyrex glass materially in the range 20° to 200° C.

2. The original expansivity of the tubing corresponded to that obtained by treating the glass at temperatures near 650° C.

3. After the expansivity of an untreated specimen of this glass had been reduced by annealing at relatively low temperatures, it was restored to its former value by retreating at temperatures near 650° C.

4. Except for certain narrow temperature intervals, a shift in the effective annealing temperature within the annealing range produced, during an annealing or disannealing, a volume change whose absolute magnitude usually exceeded quite materially that of the volume change developed between room temperature and the annealing range as the result of a change produced coincidently in the true expansivity by such a shift. The volume changes observed at a standard room temperature and caused by shifts in the effective

annealing temperature may be either the sum or difference of these two types of volume change (absolute values).

5. A sample of this glass having the maximum density so far attained by a treatment at 450° C. will on being retreated at 550° increase in volume during the annealing by an amount which approaches 50 percent or more of the cubical expansion during the heating from 20° to 500° C.; consequently, a slow rate of heating in the range 450° to 550° C. results in an average apparent thermal expansivity greatly exceeding the true value of the expansivity of the glass in this range.

6. Extreme changes in annealing procedure may produce a change as great as 10 percent in the expansivity, and this, together with the accompanying volume change, may be of some practical significance in certain cases.

7. These changes do not appear to be directly related to the process of devitrification.

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EVALUATION OF MANILA-ROPE FIBER FOR COLOR

By Genevieve Becker [1] and William D. Appel [2]

ABSTRACT

A quantitative method for the evaluation of the color of manila-rope fiber was developed at the request of the Cordage Institute and the Cordage Committee of the Federal Specifications Board. Spectral reflection and colorimetric measurements showed that the variations in color correspond chiefly to variations in luminous reflectance. The reflectance at wave length 500 mμ, which is obtainable with relatively simple apparatus, was found to be sufficient for the grading of the fiber for color. The fibers in a cross section of the rope are cut into lengths of 1.5 to 2.5 mm, mixed, extracted with petroleum ether, and spread out to give a smooth surface. The ratio of the reflectance of this surface to that of the usual white standard magnesium oxide surface for light of wave length 500 mμ (when the two surfaces are in effect equally illuminated at an angle of approximately 45° and viewed in a line approximately perpendicular to the surfaces) multiplied by 100 gives the numerical value, "Becker value", for the rope. The Becker value of the commercial ropes tested varied from 29.0 to 51.0. Before removal of the lubricant the values were from 8 to 16 units lower. The value obtained for a single specimen taken from a coil of rope was found to be within two units of the average value for several specimens. The method is prescribed in the latest revision of the Federal specification for manila rope.

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I. INTRODUCTION

Manila rope is used extensively throughout the United States in private activities. The military, naval, and engineering establishments of the United States Government require considerable quantities of manila rope in their regular work. Human safety frequently depends upon the quality of the rope.

The official Philippine Island government grading of abacá fiber from which manila rope is made is based upon three characteristics: strength, "cleaning", and color.[3] In general, the greater the strength of the fiber the stronger the rope made from it and the cleaner the fiber the more resistant the rope to decay.[4] The different grades vary in color from light straw to dark brownish or purplish.

[1] Research Associate at the Bureau of Standards for the Cordage Institute.
[2] Chief, Textile Section, Bureau of Standards.
[3] Fiber Standardization Board administrative order no. 7. Determination and Description of the Official Standards for the Various Commercial Grades of Certain Philippine Fibers. 16 pp. 1932. Department of Agriculture and Natural Resources, Manila, P.I.
[4] M. M. Saleeby: The Standard Grades of Abacá, Their Causes, Origin, and Influence on Production. Bulletin no. 1, Fiber Standardization Board, Manila 1930.

The Federal Specification for Manila Rope used from 1929 to 1933 [5] prescribed the grades and the proportions of these grades to be used in rope for Government purchase. In view of the impracticability of inspection of the fiber going into rope for Government contracts and the impossibility of determining the grades of fiber by visual examination of the finished rope, the Cordage Institute and the Cordage Committee of the Federal Specifications Board joined in a request that the Bureau of Standards develop a method for the evaluation of the color of the fiber in rope, for use as a measure of the grade of the fiber. The intention was to prescribe this method in a revision of the Federal specification. It was also anticipated that the method would prove to be of value to the industry in the standardization of its product.

This paper is one outcome of the request. It discusses the preparation of specimens of the fiber for color measurement, reports the results of spectrophotometric and colorimetric measurements of the fiber in ropes of different grades, and describes a relatively simple method for evaluating one element of the color which appears adequate for the purpose. The effects of the lubricant in rope and its removal on the color of the fiber are shown. Methods of sampling are discussed and the reproducibility of results is indicated.

This work was not concerned with the relation between the color of fiber and the serviceability of rope made from it. The serviceability of rope obviously depends upon its strength and its resistance to deterioration influences such as light, heat, wetting and drying, organisms, repeated flexing, loading and unloading. Although the opinion has been held in the industry that rope made from dark grades of fiber is less serviceable than that made from lighter grades, recent experiments carried out by the Navy Department indicate that some darker rope may be as serviceable as the Navy standard. It should be remembered that abacá fiber may be bleached, though current practice is not to bleach it.

The proposed method has been incorporated in the latest revision of the Federal specification [6] and is being used by a number of cordage manufacturers.

The work reported here was made possible by the establishment of a research associate at the Bureau of Standards by the Cordage Institute, J. S. McDaniel, secretary, and was greatly facilitated by the generous cooperation of 12 cordage manufacturers and the Boston Navy Yard in furnishing the rope required for experiments. Dr. K. S. Gibson and Dr. Deane B. Judd of the colorimetry section of the Bureau of Standards have made numerous valuable suggestions in the course of the work. Their help is gratefully acknowledged.

II. PREPARATION OF SPECIMEN

Several methods for preparing the rope fiber for measurement were considered. It is possible to measure the average color of a section of the rope, coiled in such a way as to give a measurable surface, or of short lengths of rope laid side by side, or even of a small area on the rope. However, the results obtained would depend upon the construction of the rope, the yarn size, number of strands, and amount of twist. Further, any dirt or dust on the rope would materially alter

[5] F.S. No. 61b, Rope, Manila, 5 p. 1929. U.S. Government Printing Office, Washington, D.C.
[6] F.S. No. T-R-601, Rope, Manila, 8 p. Mar. 7, 1933. U.S. Government Printing Office, Washington, D.C.

the results. This would be the method to use if the color of the surface of the rope itself were to be measured, but the color of the fiber, rather than the color of the rope, is of primary interest.

A second method for preparing the rope would be to untwist the yarns and lay the fibers out in a mat. This did not prove satisfactory unless the fibers were soaked in water to remove the twist from them. Even then, a flat, smooth, readily duplicable surface was not obtained.

A third method is to cut the fibers into short lengths. This proved to be satisfactory and was the method adopted. The colored marker is removed from a short piece of rope and sections from 1.5 to 2.5 mm long are cut at right angles to the long axis of the rope by means of a rotating disk meat cutter. The fibers thus obtained are mixed and bottled.

This specimen is representative of all of the fibers in the cross section of the rope. A minimum of rope is required since 8 g of the cut fiber is a sufficient quantity for measurement.

A portion of the fiber is placed in a dull-black receptacle at least 4 mm deep. By using the proper quantity of fiber and smoothing the surface with a spatula, the receptacle is filled and a surface effectively uniform and reproducible is obtained.

Spectral reflectance measurements of different surfaces prepared from the same lot of fiber were found to be in good agreement. (See fig. 1 and the next section of this paper.) Doubling the thickness of the layer of fiber measured did not change the values obtained. A glass cover placed over the fiber to prevent disturbance of the sample during measurement was tried, but it was found to be unnecessary if reasonable care were used to avoid jarring the specimen during measurement.

Special attention was given to the effect of variation in the length of the fibers. Distinctly lower values for the spectral reflectance were obtained with fibers cut to lengths of 5 to 6 mm. The long fibers gave a less satisfactory surface, but the short fibers required a longer time and much more care in cutting. Lengths of 1.5 to 2.5 mm were found to be reasonable satisfactory from all points of view and are prescribed for the standard procedure.

III. SPECTROPHOTOMETRIC STUDIES

Curves showing the spectral reflectance of specimens of fiber from very light, medium, and very dark 1-inch manila ropes are given in figure 1. The specimens were prepared by the method already outlined. They were not extracted to remove lubricant as provided for in the final method. The reflectance of the specimen relative to that of a standard white magnesium oxide (MgO) surface [7] is plotted as a function of the wave length of light. Fresh surfaces from the same specimens of fiber were prepared and measured at several different times. The results of each series of measurements are represented in figure 1 by circles of the same size. The curves are drawn on the basis of all of the data except those represented by the largest circles, to be referred to later. The Koenig-Martens spectrophotometer [8]

[7] Directions for the preparation of this surface are obtainable from the colorimetry section, Bureau of Standards. According to the International Critical Tables, vol. 7, p. 262, the ratio of total reflected to total incident light from MgO is 97 percent. Preston (Trans. Optical Soc. (London), vol. 31, p. 26, 1929–30) gives the "total factor under diffused light" as 0.974. The selectivity of MgO has been found to be negligible by Priest (J. Optical Soc. Am., vol. 20, p. 156, April 1930).

[8] H. J. McNicholas. Equipment for Routine Spectral Transmission and Reflection Measurements. B.S. Jour. Research, vol. 1 (R.P. 30), p. 703. November 1928.

was used. The illumination of specimen and standard was effectively equal and completely diffused and the direction in which the reflectance was measured was perpendicular to the plane of the surfaces of specimen and standard. The results were furnished by the colorimetry section of the Bureau.[9]

The reproducibility of the surface of the specimen with respect to its reflectance is shown by the agreement in the results of the several series of measurements represented in figure 1.

The results of a single series of observations on the same specimens using the Martens photometer and auxiliary equipment in the textile section of the Bureau[10] are indicated in figure 1 by the largest circles. They represent the reflectance relative to magnesium oxide at seven

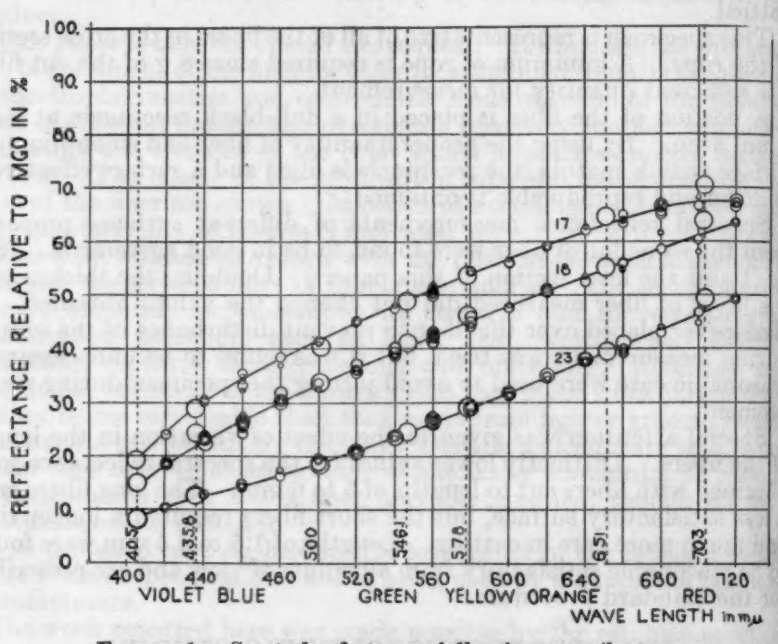

FIGURE 1.—*Spectral reflectance of fiber from manila rope.*

No. 17 was the lightest 1-inch rope tested, no. 23 the darkest, and no. 18 was intermediate in color. Fresh surfaces from the same specimens of fiber were prepared and measured at several different times. The results of each series of measurements are represented by circles of the same size. All circles except the largest represent measurements made by the colorimetry section with the Koenig-Martens spectrophotometer, using diffuse illumination. The largest circles represent measurements using the Martens photometer equipment and 45° illumination.

wave lengths when specimen and standard white are in effect equally illuminated at an angle of approximately 45° and the line of sight is approximately perpendicular to the surfaces.

In general, the data obtained with the relatively simple Martens photometer equipment are in good agreement with those from the colorimetry section even though the illumination was a directed beam at 45° instead of being completely diffused. The curves show that the reflectance of the rope fiber does not change rapidly with changes in wave length in the visible spectrum. For these reasons, the measurements at the seven wave lengths were considered satisfactory for

[9] Unpublished report. B.S. Test no. 431a-43. Mar. 25, 1932.

[10] Wm. D. Appel, A Method for Measuring the Color of Textiles. Am. Dyestuff Reptr., vol. 17, p. 49, Jan. 23, 1928.

a study of the variations in spectral reflectance of fiber from commercial ropes.

The results of measurements made with the Martens photometer equipment on the fiber from twenty-five 1-inch manila ropes, prepared as previously described but not extracted, are shown in figure 2. The ropes are the products of 13 manufacturers and include the several grades recognized by the industry. It will be noticed that the curves are of the same general shape. Similar results were obtained for the fibers from ropes of other sizes.

These curves suggested that the reflectance of the specimen relative to that of a magnesium-oxide surface for light of a single wave length, say 500 mμ, might serve as a satisfactory measure of the grade of the rope fibers.

IV. SCALE FOR GRADING ROPE FIBER WITH RESPECT TO COLOR

The color of a rope-fiber specimen depends not only upon the spectral reflectance as represented in figures 1 and 2, but it also depends upon the character of the illuminant and the eye of the observer. Assuming a standard illuminant and a standard observer, it is possible to calculate from the spectral reflectance three numbers which will adequately specify the color.[11] Any one of several triads of numbers might be used for this specification. Those used here are: (1) The reflectance of the specimen relative to that of the standard white for 31 wave lengths in the visible spectrum weighted with respect to visibility, called here the "luminous reflectance"; (2) the value of the "red" coordinate [12]; and (3) the value of the "green" coordinate. The value of the "blue" coordinate is not essential to the representation of the color because it is related to the red and green coordinates according to the equation: blue = 1 − (red + green).

The specifications for the colors of the specimens whose spectral-reflectance curves are given in figure 1, were calculated by the method outlined in the Report of the Committee on Colorimetry, Optical Society of America, pages 580–581,[13] assuming the prime-basic stimulus to be Abbot-Priest sunlight and the eye to be that represented in the Optical Society of America "excitation" curves in their extrapolated form.[14] The results are given in table 1.

TABLE 1.—*Specifications* [a] *for the colors of specimens of fibers from light, intermediate, and dark manila rope*

Specimen no.	Luminous reflectance		Red coordinate		Green coordinate	
	A [1]	*B* [2]	*A*	*B*	*A*	*B*
17	0.503	0.501	0.399	0.404	0.363	0.364
18	.417	.425	.409	.406	.365	.364
23	.260	.260	.433	.432	.365	.365

[1] Data in columns A are calculated from measurements at 20 mμ intervals throughout the visible spectrum with the Koenig-Martens spectrophotometer and diffused illumination.

[2] Data in columns B are calculated from measuresments at 7 wave lengths obtained with the Martens photometer equipment and 45° illumination.

[a] All values are computed with Abbot-Priest Sunlight as prime-basic stimulus.

[11] The discussion of the broad subject of colorimetry is not within the scope of this paper. The following reference may prove helpful: Report of Committee on Colorimetry, L. T. Troland, chairman, J. Optical Soc. Am., vol. 6, p. 527, 1922.

[12] See p. 547–553 of the reference given in footnote 11. See Deane B. Judd, Chromaticity sensibility to stimulus differences. J. Optical Soc. Am., vol. 22, pp. 72–108, 1932, in which the red and green coordinates are used.

[13] See footnote 11, p. 814.

[14] Deane B. Judd, Reduction of Data on Mixture of Color Stimuli, B.S.Jour. Research vol. 4 (R.P. 163), pp. 524–525, table 1, April 1930.

Similar results calculated on the basis of the spectral reflectance at the seven wave lengths, represented by the large circles in figure 1, are also given in table 1.[15]

The agreement between the results obtained from the more nearly complete spectral reflectance data and from the seven wave lengths only, justify the use of data of the latter type for evaluating the colors of the rope fibers represented in figure 2.

The results obtained by several methods for the evaluation of the colors of the fibers of manila ropes are given in figure 3. The numbers of the specimens from the 25 ropes whose spectral reflectances are given in figure 2, are arranged at the bottom of figure 3, in the order of the appearance of the specimens, from light to dark. This

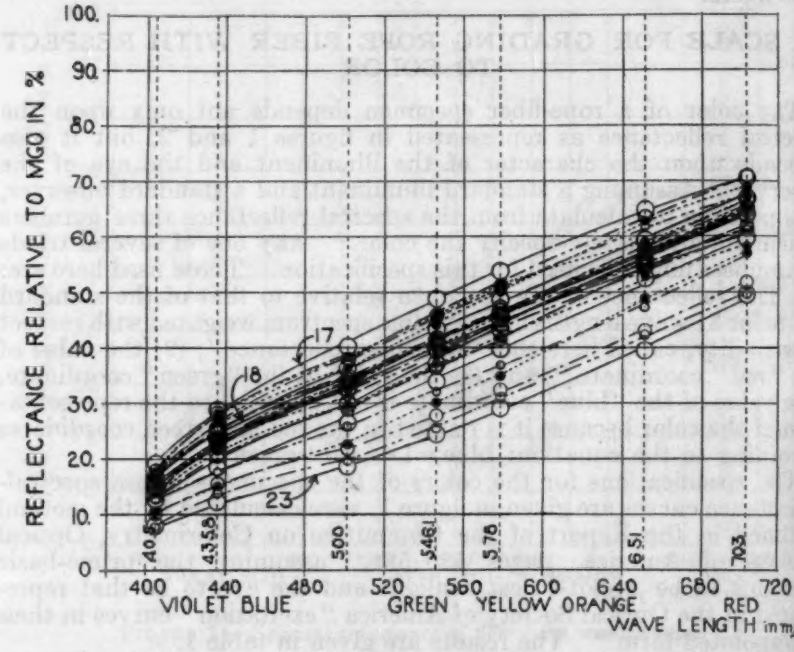

FIGURE 2.—*Spectral reflectance of fiber from 25 samples of 1-inch manila rope from 13 manufacturers*

Specimens numbers 17, 18, and 23, representing light, intermediate, and dark fiber, were also measured at every 20 millimicrons as shown in figure 1.

order is based upon the considered judgment of two observers who have had experience in judging colors. It should be noted that it was extremely difficult in some instances to decide which specimens were darker and which lighter among as many as 3 or 4 listed in order

[15] The "excitation" values used in this computation were derived by Dr. Deane B. Judd. Abbot-Priest sunlight is taken as the prime-basic stimulus. The Optical Society of America "excitation" curves in their extrapolated form are used as the basis for the derived "excitation" values. Judd states in his unpublished report to the textile section of the Bureau of Standards, dated Dec. 9, 1929: "If these values are used in the usual routine way for the computation of trilinear coordinates (r, g, b), and reflectance for the prime stimulus, the results will be exactly those found by computing on the basis of the O.S.A. "excitation" curves for an hypothetical sample whose reflection function in the neighborhood of the wavel engths specified is constant. The wave-length regions of constant spectral reflectance extend in each case half-way on the wavelength scale toward the next wave length specified. To what extent the trilinear coordinates of such a sample may be expected to differ from those of actual samples remains to be shown by actual trial. It is certain, however, that in such case as justify conclusions from spectral reflectances at these 7 wave lengths, the application of these "excitation" values will materially simplify the drawing and statement of the conclusions."

in the figure. The specimens were spread out side by side on a plane gray surface for visual comparison and were examined in north light, a pair at a time. The surface of each specimen viewed was about 1 by 2 centimeters in size.

The "luminous reflectance" and the "red" coordinates for the specimens calculated from the spectral reflectance at seven wave lengths are plotted in figure 3. The "green" coordinates of these 25 specimens show a maximum variation from 0.361 to 0.367, which is negligible. For this reason they were not plotted. The colors of the rope fibers vary from light to dark (measured by "luminous reflectance") and coincidentally they become slightly redder (measured by the "red" coordinate).

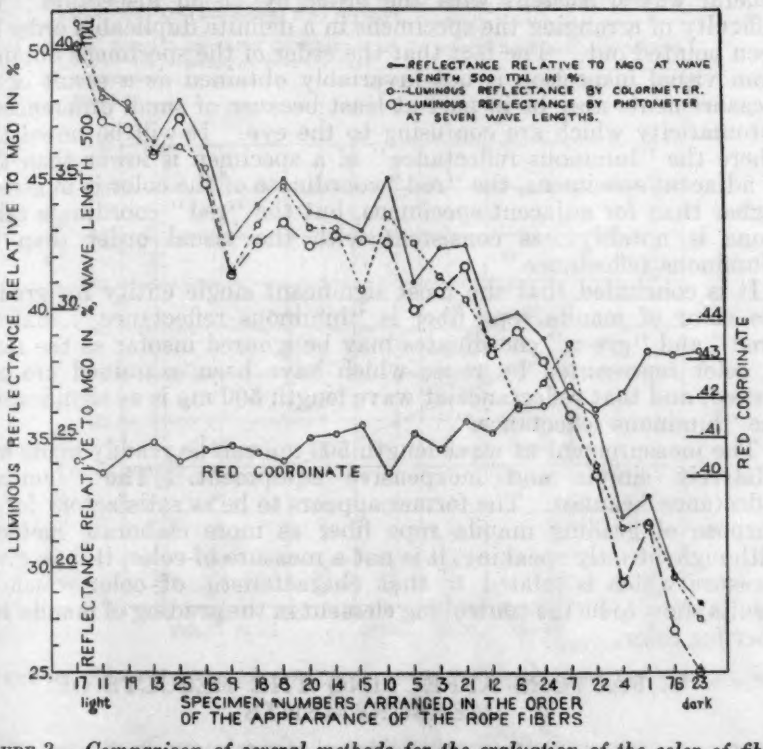

FIGURE 3.—*Comparison of several methods for the evaluation of the color of fibers from manila ropes*

The specifications of the colors can be readily obtained by the use of certain colorimeters as well as from the spectrophotometric data. Trial was made of the disk mixture colorimeter found by Nickerson [16] to be especially useful for grading raw cotton and other agricultural products. Munsell disks numbers YR 7/6, Y 8/8, N 8/, and N 3/ were used as standards.[17] The specifications of the colors were calculated from the spectral reflectances of the disks and the area of each

[16] Dorothy Nickerson, A Colorimeter for Use With Disk Mixture. J. Optical Soc. Am., vol. 21, p. 640, 1931; A Method for Determining the Color of Agricultural Products. U.S. Dept. Agr. Tech. Bull. no. 154, 32 pp., 1929; and Application of Color Measurement in the Grading of Agricultural Products. U.S. Dept. of Agr. Bur. Agr. Econ. Prelim. Rept. 36 pp. Mimeographed, January 1932.

[17] Munsell Book of Color 1929; and A. H. Munsell, A Color Notation. 1926, 7th ed. Munsell Color Co., Inc., Baltimore, Md.

disk required in rotary mixture to match the colors of the specimens. The values for "luminous reflectance by colorimeter", given in figure 3, were obtained in this way. The "red" and "green" coordinates obtained by the use of the colorimeter lead to the same conclusions as those obtained from the spectral-reflectance data, and consequently need not be reported.

The reflectance of each specimen relative to the reflectance of the white magnesium oxide surface at wave length approximately 500 $m\mu$ [18] (see fig. 2) is also plotted in figure 3.

It will be seen that the "luminous reflectance", "luminous reflectance by colorimeter", and "reflectance at wave length 500 $m\mu$", for each specimen are reasonably consistent with one another and in a general way consistent with the order by visual inspection. The difficulty of arranging the specimens in a definite duplicable order has been pointed out. The fact that the order of the specimens obtained from visual inspection is not invariably obtained as a result of the measurements may be in part at least because of small differences in chromaticity which are confusing to the eye. It will be noted that where the "luminous reflectance" of a specimen is lower than that of adjacent specimens, the "red" coordinate of the color is in general higher than for adjacent specimens, but the "red" coordinate taken alone is notably less consistent with the visual order than the "luminous reflectance."

It is concluded that the most significant single entity for grading the color of manila rope fiber is "luminous reflectance", that the "red" and "green" coordinates may be ignored insofar as the range in color represented by ropes which have been examined are concerned, and that reflectance at wave length 500 $m\mu$ is as significant as the "luminous reflectance."

The measurement at wave length 500 $m\mu$ can be readily made with relatively simple and inexpensive equipment. The "luminous reflectance" cannot. The former appears to be as satisfactory for the purpose of grading manila rope fiber as more elaborate methods. Although, strictly speaking, it is not a measure of color, it does give a measure which is related to that characteristic of color which the results show to be the controlling element in the grading of manila rope fiber for color.

V. FACTORS AFFECTING THE RESULTS OF MEASUREMENTS

Most rope contains from 10 to 15 percent of an oil or other lubricant. This lubricant affects the color to various degrees depending upon the original color of the lubricant, the amount of dust it has picked up, and the extent to which it has been bleached or darkened through exposure to light and air. Since the proposed measurements are intended to show the color of the fiber before lubrication rather than as it actually occurs in rope, the cut fiber is extracted for 2 hours with petroleum ether in a Soxhlet extraction apparatus to remove the lubricant. In order to insure that the extraction does not remove colored materials

[18] Measurements at approximately 500 $m\mu$ are conveniently obtained by illuminating the specimen and standard with light from a mazda C lamp operating near 2,848° K (the 300- or 500-watt lamps operating at normal voltage will be sufficiently close to this) and viewing them through Wratten filter no. 75 placed over the eyepiece of the photometer. (This filter is obtainable from the Eastman Kodak Co., Rochester, N.Y.) The filter isolates a relatively narrow spectral band. The exact wave length to assign to the measurement depends upon the color temperature of the incandescent lamp, the spectral transmission of the filter, and the visibility function of the observer.

other than the lubricant, the effect of the extraction upon fiber which had not been lubricated was studied. No significant change in reflectance at wave length 500 mμ resulted from the extraction.

TABLE 2.—*The effect of the lubricant and its extraction upon the reflectance of abacá fiber*

Sample no.	Material measured	Reflectance at wave length 500 mμ relative to MgO
		Percent
1	Original fiber	58.8
2	Original fiber+12 percent of its weight of oil (90 percent mineral oil+10 percent wool olein). Oil remained on fiber 9½ days	51.9
3	No. 2 extracted	57.0
4	Original fiber+12 percent of its weight of oil (75 percent mineral oil+25 percent degras). Oil remained on fiber 9½ days	51.0
5	No. 4 extracted	57.0

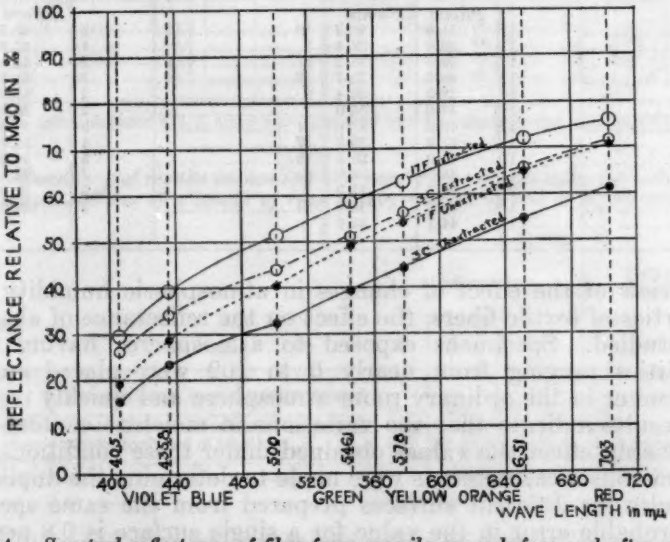

FIGURE 4.—*Spectral reflectance of fiber from manila ropes before and after extraction of lubricant.*

The results of experiments in which fiber of known reflectance was lubricated, measured, extracted, and again measured are given in table 2. The lubricants used decreased the reflectance considerably and the extraction did not completely restore the fiber to its original reflectance value. The extent to which the original value will be approached in any particular case will depend upon such factors as the susceptibility of the lubricant to oxidation or polymerization.

The extent to which extraction changes the spectral reflectance for typical rope fibers is shown in figure 4.

The reflectance at wave length 500 mμ of fiber specimens from 1-inch ropes before and after extraction are given in table 3. The order of decreasing reflectance is not exactly the same before and after extraction. The nominal grade of the ropes, as recognized in the trade,

is indicated in the table. In general, the lower grades have lower reflectance values.

Data similar to those in table 3 were otbained for a series of ½-inch and 5/16-inch manila ropes from the same manufacturers. The range in reflectance at 500 mμ for the twenty-five ½-inch ropes in the series before extraction was from 42.5 to 19.7 and for the twenty 5/16-inch ropes from 44.3 to 18.9.

TABLE 3.—*Reflectance at wave length 500 mμ of 25 samples of 1-inch manila rope from 13 different manufacturers. Results on both extracted and unextracted specimens are given*

Specimen no.	Nominal grade of rope	Reflectance at wave length 500 mμ relative to MgO		Specimen no.	Nominal grade of rope	Reflectance at wave length 500 mμ relative to MgO	
		Extracted	Unextracted			Extracted	Unextracted
		Percent	*Percent*			*Percent*	*Percent*
17	1	51.0	40.2	10	3	43.3	35.0
11	1	50.0	38.4	3	1	42.9	32.3
16	1	49.6	36.2	21	2	42.0	32.4
9	1	48.9	32.7	12	2	41.7	29.5
13	1	48.3	36.4	6	2	41.3	29.8
18	1	48.0	34.0	7	2	39.8	28.5
19	1	47.2	37.6	24	2	36.4	28.8
15	1	47.0	33.0	22	4	34.9	25.8
14	1	46.0	33.5	76	3	34.9	19.7
25	1	45.7	38.0	4	3	33.3	21.9
20	3	44.8	33.7	1	3	33.0	22.7
8	1	44.6	35.0	23	3	29.0	18.6
5	1	44.1	31.0				

In view of the effect of changes in atmospheric humidity on the properties of textile fibers, the effect on the reflectance of abacá fiber was studied. Specimens exposed to atmospheres having relative humidities ranging from nearly 0 to 100 were placed under the photometer in the ordinary room atmosphere and quickly measured. The results indicate that the variations in moisture content do not appreciably affect the values obtained under these conditions.

Numerous measurements were made to determine the duplicability of results for different surfaces prepared from the same specimens. The probable error in the value for a single surface is 0.8 percent of the average value for the surfaces.

The number of specimens to be taken from any coil [19] of rope in order to obtain a fair average reflectance value for the coil received attention. Half coils and portions from coils of first-grade 1-inch manila rope were used. In the study of the half coils, specimens for measurement were taken at equal intervals of the 600 feet of rope. In the study of the 60-foot lengths which were taken from the ends and center of each of the coils, specimens were taken at each end of these lengths. The reflectance values for specimens taken from five places in the half coils and from each end of the 60-foot lengths are given in table 4. The values given for the maximum variation in each of the lengths are the differences between the highest and lowest values obtained for the specimens in that length. Table 5 gives the average of the results for the 5 or 6 measurements on each coil and

[19] In commercial usage the standard length of a coil of 1-inch rope is 1,200 feet.

indicates how closely 3 measurements, 2 measurements, or a single measurement will approach the average value. If the average of the 5 or 6 measurements obtained for each coil is taken to be the true value for that coil then a single measurement would be well within 2 units of its true value.

TABLE 4.—*Values of reflectance at wave length 500 mμ for specimens taken at 3 to 6 places in a coil of rope*

Coil no.	Distance in feet from starting end of coil										Maximum variation
	0	60	150	300	450	570	600	630	1,140	1,200	
1	49.9	51.2	------	------	------	50.8	------	50.8	49.6	50.5	1.6
2	49.8	49.5	------	------	------	49.2	------	49.2	49.7	48.6	1.2
3	47.1	47.0	------	------	------	47.9	------	48.0	46.7	47.6	1.3
4	47.8	47.6	------	------	------	46.2	------	47.5	46.3	47.7	1.6
Half coil no.:											
1	44.7	------	44.1	44.5	45.5	------	44.5	------	------	------	1.4
2	44.7	------	45.8	46.8	44.5	------	45.3	------	------	------	2.3
3	44.4	------	46.3	47.2	46.7	------	44.8	------	------	------	2.8
Coil no.[1]:											
5	49.1	------	------	------	------	------	48.3	------	------	48.9	.8
6	45.0	------	------	------	------	------	45.1	------	------	46.8	1.8
7	40.3	------	------	------	------	------	39.5	------	------	39.0	1.3
8	53.8	------	------	------	------	------	53.2	------	------	51.6	2.2

[1] Samples from coils numbered 5, 6, 7, and 8 were furnished by 1 manufacturer and represent 4 qualities of rope.

TABLE 5.—*Summary of results indicating how nearly the average value for reflectance at wave length 500 mμ of a length of rope is approached by one or a few measurements*

	Coil number				Half coil number		
	1	2	3	4	1	2	3
Average of 5 or 6 measurements (equidistantly spaced throughout)	50.5	49.3	47.4	47.2	44.7	45.4	45.9
Average of 3 measurements (2 ends and center of length)	50.4	49.2	47.5	47.2	44.6	45.6	45.5
Average of 2 measurements (each end of length)	50.2	49.2	47.4	47.8	44.6	45.0	44.6
1 measurement—1 end	49.9	49.8	47.1	47.8	44.7	44.7	44.4
1 measurement—center	50.8	49.2	47.9	46.2	44.5	46.8	47.2

The sampling of rope at any considerable number of places would be costly both in rope wasted and the time and labor of the tests. There seems to be no more reason for taking a large number of samples for color than for taking a large number for breaking strength. Breaking strength is usually measured by testing a single specimen.

VI. STANDARD PROCEDURE

The procedure described here was proposed to the Cordage Committee of the Federal Specifications Board and has been incorporated in the latest revision of the Federal specification for manila rope.[20] The necessary equipment[21] can be assembled in any well-organized laboratory. At least one firm is prepared to supply equipment, specially built for the purpose.

[20] See footnote 6, p. 812.

[21] Working drawings of photometric equipment suitable for the purpose described and directions for its use are available on request to Textile Section, Bureau of Standards, Washington, D.C.

All of the fibers in a representative cross section of the rope are taken for test. These fibers are cut into lengths of 1.5 to 2.5 mm. This may be done with scissors, tinner's snips, or a sharp knife, but more conveniently with a meat cutter having a revolving disk blade. The cut fibers are thoroughly mixed and an 8-g portion is extracted in a Soxhlet apparatus for 2 hours with petroleum ether. The extracted fibers are spread on a clean filter paper and allowed to dry in the air over night. The reflectance of the fiber is measured the following day.

The fiber is placed in a black receptacle not less than 4 mm deep and alternately pressed and smoothed with a spatula until a smooth, flat surface is obtained.

The ratio of the reflectance of this surface to that of the usual white standard magnesium oxide surface when the two are in effect equally illuminated at an angle of approximately 45° and viewed in a line approximately perpendicular to the surfaces is measured with a suitable photometer, at wave length approximately 500 mμ. This ratio multiplied by 100 is the reflectance of the fiber in percent relative to that of magnesium oxide. This value has been designated the "Becker value" in the Federal specification for manila rope.

WASHINGTON, September 16, 1933.

U.S. Department of Commerce, Bureau of Standards

RESEARCH PAPER RP628

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SPECTRAL REFLECTANCE OF THE PHILIPPINE ISLAND GOVERNMENT STANDARDS FOR ABACÁ FIBER

By Genevieve Becker [1]

ABSTRACT

This paper reports the results of spectral reflection measurements of one set of the official standards for the grades of abacá used in cordage. The results provide a quantitative record of those characteristics of the fiber on which the color depends. They should be of permanent value since the grading is largely on the basis of color. They suggest the possibility of using quantitative reflectance measurements in the Philippine Islands to supplement, if not to replace, the present method of grading abacá for color. Three specimens representing the base, tip, and middle of each of 10 standard samples were measured at seven wave lengths. The average values found for the spectral reflectance at wave length 500 mμ, which are illustrative of the results, follow: Superior current 59.3, good current 54.9, midway 49.9, 25 percent over fair current 46.5, streaky two 45.4, streaky three 33.5, fair current 42.5, superior seconds 40.0, soft seconds 31.3, soft brown 21.5. The highest and lowest measurement for a given standard differ by from 2 to 13 units and there is decided overlapping in the measurements for some of the different grades.

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I. INTRODUCTION

A method for evaluating the color of abacá fiber in rope, by means of spectral reflection measurements has been described.[2] The method is used in the revised specification for manila rope [3] which prescribes minimum reflectance values for rope for government purchase. Formerly the permissible grades of fiber and proportions of these grades were specified.[4] Thus it becomes of interest to know the reflectance values for the commercial grades of abacá.

The grading of abacá fiber is done in the Philippine Islands where most of the fiber of commerce is grown. It consists of practical hand tests and visual examination by inspectors of the Fiber Standardization Board. The grade of the fiber depends upon three factors: Strength, "cleaning," and color. A certain basic strength is required for all abacá included in the standard grades. Cleaning determines the group of grades under which the fiber is classified. Color determines the actual grade of the fiber within that group. The three

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[2] Evaluation of Manila Rope Fiber for Color, Genevieve Becker and Wm. D. Appel, B.S.Jour. Research, vol. 11 (RP 627), p. 811.
[3] F.S. no. T-R-601, Rope, Manila, 8 p., Mar. 7, 1933. Government Printing Office, Washington, D.C.
[4] F.S. no. 61b, Rope, Manila, 5 p., 1929, Government Printing Office, Washington, D.C.

properties are closely related, for the kind and extent of cleaning affect both tensile strength and color. The standard grades of abacá fiber are described in administrative order no. 7 of the Fiber Standardization Board.[5] They are represented by standard samples obtainable from the Board.

This paper reports the results of spectral-reflection measurements of one set of the official standards for the grades of abacá used in cordage. The results provide a quantitative record of those characteristics of the fiber on which the color depends and therefore they should be of permanent value. They suggest the possibility of using quantitative spectral reflectance measurements in the Philippine Islands to supplement, if not to replace, the present method of grading abacá for color.

This work was not concerned with the relation between the color of fiber and the serviceability of rope made from it.

The work was undertaken at the suggestion of the Cordage Institute, J. S. McDaniel, secretary, and was made possible by the financial support of the institute.

II. MATERIALS

A set of 10 samples bearing the official Philippine Island Government stamp was provided by the Cordage Institute on February 16, 1933. These samples represent the Philippine Island Government standards for the following commercial fiber grades:

Letter designation	Name of grade
AB	Superior current
CD	Good current
E	Midway
F	25 percent over fair current
S2	Streaky two
S3	Streaky three
I	Fair current
J1	Superior seconds
G	Soft seconds
H	Soft brown

The samples were in the form of bundles of fiber ranging from 5 feet 2 inches to 7 feet in length and approximately 8 inches in circumference. Microscopic examination of representative fibers from the samples showed that the diameters of individual fibers varied from 0.08 to 0.50 mm. Samples representing the lower grades of fiber exhibited considerable variation in color; the upper grades were more nearly uniform in this respect.

III. PROCEDURE

Three specimens, (a), (b), and (c), were taken from each of the standard samples. Specimen (a) was taken from the extreme base of the standard sample; specimen (b), because of considerable fraying out and the broken condition of the fibers at this end, was taken at a distance of about 1 foot from the extreme tip; specimen (c) was taken at a distance half-way between specimens (a) and (b). Each specimen weighed about 12 ounces and was a complete cross-section of the

[5] Fiber Standardization Board administrative order no. 7. Determination and Description of the Official Standards for the Various Commercial Grades of Certain Philippine Fibers. 16 pp. 1932. Department of Agriculture and Natural Resources, Manila, P.I.

bundle. Each was reduced to a finely chopped condition by cutting the fibers to lengths of 1.5 to 2.5 mm with a meat cutter having a revolving blade. The chopped fibers were thoroughly mixed, bottled, and kept in a dark place until measured.

The equipment used for determining the spectral reflectance of the fiber [6] and the method for preparing the fiber surface for measurement have already been described in detail.[7] The method consists essentially of placing the fiber in a black container approximately 4 mm deep, pressing and smoothing it with a spatula to obtain a flat, smooth surface. The reflectance of this surface relative to that of a standard white magnesium oxide surface was determined for light of seven wave lengths for the following conditions: (1) The sample and standard-white surface were in effect under equal illumination, (2) the angle of incidence of the light was approximately 45° and, (3) the direction in which the reflectance was measured was perpendicular to the plane of the surfaces of sample and standard. This reflectance ratio multiplied by 100 is the reflectance in percent reported in the figures and in table 1.

TABLE 1.—*Spectral reflectance of a set of the Philippine Island Government standards for abacá fiber*

[The values given are the spectral reflectance in percent relative to magnesium oxide, when sample and standard are in effect equally illuminated at an angle of approximately 45° and the line of sight is approximately perpendicular to the surfaces]

Philippine Island letter designation and name of grade	Location of specimen in the standard hank [a]	Reflectance (in percent) at wave lengths (millimicrons)						
		703	651	578	546.1	[b] 500	436.8	405
AB—Superior current	a	80.8	77.2	69.8	65.4	60.2	49.5	39.0
	b	74.5	71.7	65.9	62.6	57.8	45.9	34.0
	c	80.6	76.6	70.0	66.3	59.9	48.8	37.4
Average		78.6	75.2	68.6	64.8	59.3	48.1	36.8
CD—Good current	a	80.6	76.0	67.2	66.0	57.8	47.8	36.2
	b	69.6	66.4	59.6	55.9	49.7	40.8	29.5
	c	80.2	76.2	67.9	63.4	57.2	46.2	35.4
Average		76.8	72.9	64.9	61.8	54.9	44.9	33.7
E—Midway	a	77.2	73.0	64.2	61.2	53.3	43.4	36.8
	b	71.4	68.4	56.9	53.8	46.9	36.1	27.9
	c	76.9	71.4	61.3	56.9	49.5	39.3	32.0
Average		75.2	70.9	60.8	57.3	49.9	39.6	32.2
F—25 percent over fair current	a	74.4	69.6	59.2	55.5	48.7	38.7	29.6
	b	69.8	65.1	56.1	51.6	44.9	34.4	25.6
	c	75.0	69.4	58.2	53.2	45.8	35.3	27.6
Average		73.1	68.0	57.8	53.4	46.5	36.1	27.6
S2—Streaky two	a	74.6	68.8	59.3	54.8	49.4	38.0	29.7
	b	69.5	64.3	54.2	49.1	42.2	32.6	25.6
	c	71.8	66.6	56.6	51.6	44.7	35.1	27.7
Average		72.0	66.6	56.7	51.8	45.4	35.2	27.7

[a] Location of specimen in the standard hank: a, base; b, tip; c, middle.
[b] The values in this column are the "Becker values" for the fibers.

[6] Wm. D. Appel, A Method for Measuring the Color of Textiles. Am. Dyestuff Reptr., vol. 17, p. 49, Jan. 23, 1928.
[7] See footnote 2, p. 823.

TABLE 1.—*Spectral reflectance of a set of the Philippine Island Government standards for abacá fiber*—Continued

Philippine Island letter designation and name of grade	Location of specimen in the standard hank [a]	Reflectance (in percent) at wave lengths (millimicrons)—						
		703	651	578	546.1	[b] 500	436.8	405
S3—Streaky three	a	70.2	64.2	53.2	48.1	41.8	33.4	26.1
	b	59.8	52.0	40.7	36.5	30.0	22.4	18.0
	c	57.2	49.5	40.6	35.7	28.7	22.3	18.0
Average		62.4	55.2	44.8	40.1	33.5	26.0	20.7
I—Fair current	a	75.0	69.8	57.8	53.0	46.0	36.0	28.9
	b	71.4	64.8	53.1	44.6	40.3	30.5	24.1
	c	73.0	66.6	53.7	48.9	41.1	31.7	25.4
Average		73.1	67.1	54.9	48.8	42.5	32.7	26.1
J1—Superior seconds	a	72.2	68.6	58.0	53.0	45.4	35.8	28.4
	b	68.4	62.1	50.8	45.8	38.1	29.2	22.1
	c	69.4	62.0	49.5	44.2	36.6	27.8	22.4
Average		70.0	64.2	52.8	47.7	40.0	30.9	24.3
G—Soft seconds	a	67.4	58.8	46.3	42.1	35.4	26.0	21.6
	b	58.9	52.0	41.7	36.6	30.1	22.1	17.6
	c	60.8	52.0	40.1	35.5	28.3	20.4	16.3
Average		62.4	54.3	42.7	38.1	31.3	22.8	18.5
H—Soft brown	a	49.3	38.9	31.7	28.3	23.3	17.8	14.5
	b	44.6	36.2	29.8	26.0	21.1	15.2	12.1
	c	45.3	36.5	28.9	25.4	20.0	14.3	11.5
Average		46.4	37.2	30.1	26.6	21.5	15.8	12.7

[a] Location of specimen in the standard hank: a base; b, tip; c, middle.
[b] The values in this column are the "Becker values" for the fibers.

IV. RESULTS

The results of the measurements are recorded in numerical form in table 1. The average for the specimens from the base, tip, and middle of each standard is also given.

The average data are plotted in the form of curves in figure 1. In general, the curves have the same shape, the order of the values being that of the standard grades listed under section II of this paper, except that the values for the grade S3 are lower than those for grades I and J1.

The variation in spectral reflectance between specimens from the base, tip, and middle of the standards for the grades commercially used in rope is shown in figure 2. The reflectance of specimens from the base is usually higher than that of specimens from the tip and middle.

The maximum observed variation in spectral reflectance for each standard at each of the seven wave lengths and the overlapping between grades is illustrated in figure 3. The highest and lowest value for a given grade differ by 2 to 13 units. The great variation, 13 units, in grade S3, is a result of the very dark bundles of fiber in it which give it a streaky appearance. They account for the low value of the average spectral reflectance and the position of the curve for S3 in figure 1.

In figure 4 are plotted the reflectances at wave length 500 mμ of the specimens from each standard. The reflectance of a rope fiber at this wave length relative to that of magnesium oxide is the Becker value of the Federal Specification for manila rope.[8] The minimum

[8] See footnote 3, page 823.

values for rope for Government purchase are: 46 for rope ½ to 2 inches in nominal circumference, inclusive; 43 for rope 2¼ inches

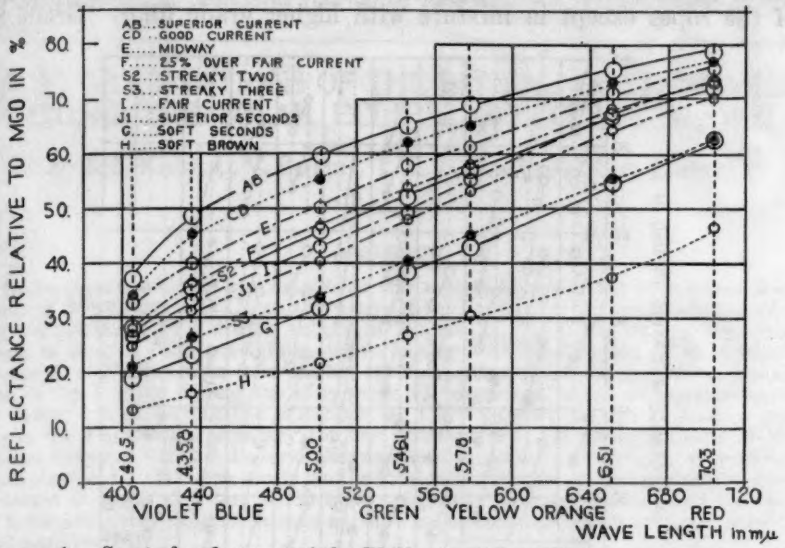

FIGURE 1.—*Spectral reflectance of the Philippine Island Government standards for abacá fiber. Each point is the average reflectance of specimens taken from the base, middle, and tip of the standards.*

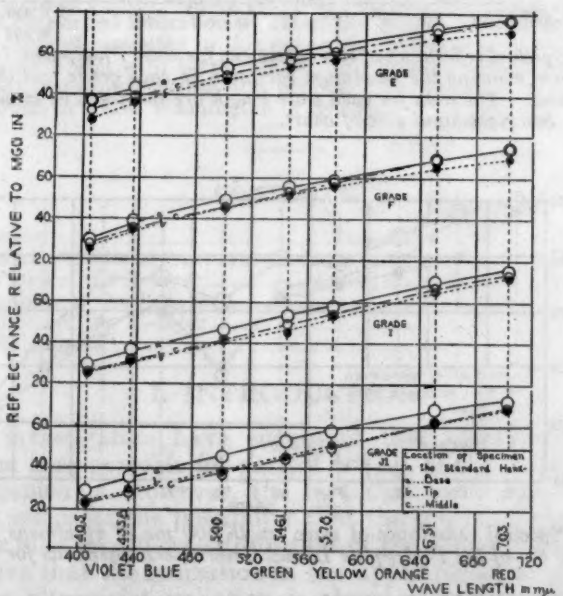

FIGURE 2.—*Spectral reflectance of the Philippine Island Government standards for the commercial grades used in manila rope, showing the variation between specimens taken from the base, middle, and tip of the standards.*

in nominal circumference and above. The average Becker values for the standards for grades commonly used in rope are: for grade

E 49.9, F 46.5, I 42.5, and J1 40.0. Thus the E and F grade standards meet the requirement for smaller ropes, but the I and J1 grade standards have average Becker values too low for use in any of the ropes except in mixture with higher grade fiber. Grade S2

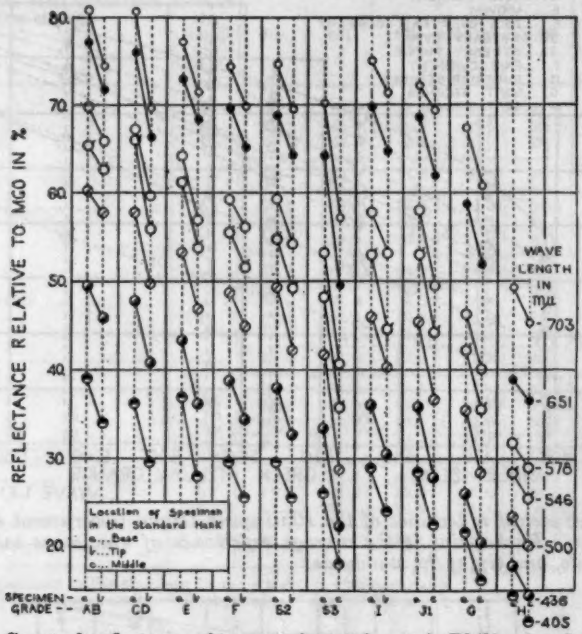

FIGURE 3.—*Spectral reflectance of two specimens for each Philippine Island Government standard showing the maximum variation in each grade and the overlapping between grades. The data for each wave length are indicated by circles of the same character. See right-hand side of chart.*

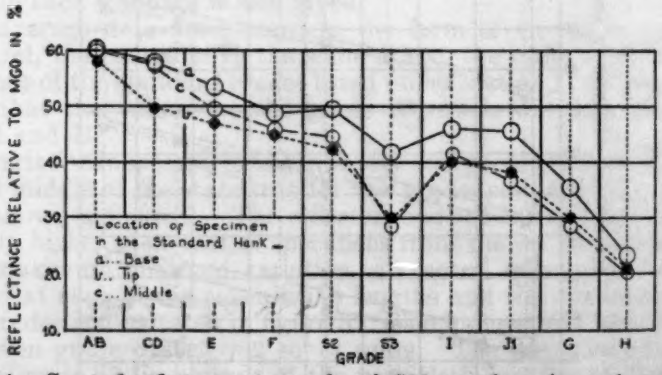

FIGURE 4.—*Spectral reflectance at wave length 500 mμ of specimens from the base, middle, and tip of the Philippine Island Government standards for abacá fiber.*

appears to be suitable for use in rope made to meet the specifications insofar as color is concerned.

It should be remembered that the fiber in commercial bales of abacá may vary more in reflectance than the fibers in the standards measured.

WASHINGTON, October 18, 1933.

U.S. DEPARTMENT OF COMMERCE, BUREAU OF STANDARDS

RESEARCH PAPER RP629

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RADIO OBSERVATIONS OF THE BUREAU OF STANDARDS DURING THE SOLAR ECLIPSE OF AUGUST 31, 1932

By S. S. Kirby, L. V. Berkner, T. R. Gilliland, and K. A. Norton

ABSTRACT

Radio observations of the heights of the several layers of the ionosphere were made at Washington, D.C., and Sydney, Nova Scotia, by the pulse method during the afternoon of the solar eclipse of August 31, 1932, and during the afternoons of several days preceding and following. At Washington three separate groups of determinations were made: (1) measurements of the maximum ionization of the E-layer during the afternoon; (2) continual series of measurements of virtual height during the afternoon at 4,200 kc/s which was ordinarily just above the F_1 critical frequency for the ordinary ray; (3) measurements of the critical frequency of the F_2-layer during the afternoon. At Sydney, determinations similar to (1) were made and continuous records of virtual height were obtained at 2,400 kc/s and 3,000 kc/s. Separate equipment was used for each of these groups of determinations so that measurements could be made rapidly and continuously.

It was found that the ionization of the E-layer decreased to about 30 percent of its normal value at the time of the eclipse maximum, the variation taking place approximately in phase with the eclipse. The ionization of the F_1 layer likewise decreased in almost exactly the same manner, reaching a value of about 40 percent of its normal ionization at about the eclipse maximum. When analyzed by the method presented in this paper, observations of other investigators are found to agree well with these results. No unusual change was evident in the F_2 critical frequency during the eclipse. No evidence of a corpuscular eclipse was found at either Washington or Sydney.

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I. INTRODUCTION

Various investigators have suggested that ultraviolet radiation from the sun is responsible for part, if not all, of the ionization in the upper atmosphere. However, the fact that more layers than one are present indicates the possibility that the source of the ionization of one layer may be different from that of the others. Some investigators believe that the ionization in the upper region is so great that most of the ultraviolet radiation is absorbed and that some other agency may be required to explain the ionization of the lower layers. It has been suggested by Professor Chapman [1] [2] in England that the lower region of ionization is caused by neutral corpuscles shot out from

[1] Chapman, Monthly Notices of R.A.S., March 1932.
[2] Appleton & Chapman, Nature, May 21, 1932.

the sun. It has been shown that such corpuscles are likely to be emitted by radiation-pressure acting upon atoms and that a velocity of about 1,600 km/s away from the sun may be attained. At present there is no observational proof that such particles are present, but if they exist and are responsible for any appreciable part of the ionization in the upper atmosphere, an eclipse of the sun should offer an opportunity to show just how important this agent is.

If ultraviolet radiation and particle bombardment were both important, we might expect the effect of one to be cut off before the other because of their different velocities, and changes during the eclipse to be much more abrupt and clear cut than the changes noted from day to night. Calculations indicate that the particle eclipse should occur approximately 2 hours before the light eclipse. According to Chapman's calculations on the basis of a particle velocity of 1,600 km/s, the corpuscular eclipse track would lie to the east of the optical-eclipse track, and should be observed in northeastern North America.

In order to study this effect, observations were made in Washington, D.C., and Sydney, Nova Scotia, the latter lying within the area of the suggested corpuscular eclipse. As Washington was to the west and Sydney to the east of the optical eclipse, and both points were subject to approximately 90 percent optical totality, the magnitude of changes at the two places due solely to ionizing sources travelling from the sun at the velocity of light should be of the same order.

An expedition comprising Messrs. Gilliland, Norton, and Carnes proceeded to Sydney. The equipment was taken in two laboratory trucks. Observations were made at Washington by Messrs. Kirby and Berkner.

In order to study possible optical and corpuscular effects, it was decided to make a series of determinations of the maximum ionizations of the various layers when facilities permitted and lacking these, to make continuous records of virtual heights at frequencies so selected as to give as much information as possible regarding the changes of such maximum ionizations. The critical frequency of a layer has been defined as the lowest frequency which penetrates the layer. This frequency is a measure of the maximum ionization. These measurements, therefore, involved the determination of a series of critical frequencies, each determination requiring a series of from 5 to 10 measurements. This procedure has been completely described elsewhere.[3]

The general method used was that of Breit and Tuve [4] as adapted and described [5 6 7] in previous Bureau of Standards publications. For the somewhat specialized apparatus of the expedition, two types of oscillograph were employed for measurements. A cathode-ray tube was used for visual work and manual measurements while a string oscillograph was used for continuous photographic recording.

A new method was employed for measuring the pulse-retardation time on the cathode-ray oscillograph. The sweep-circuit voltage was

[3] Kirby, Berkner, and Stuart, Studies of the ionosphere and their application to radio transmission, B.S.Jour. Research, vol. 12, January 1934.
[4] Breit and Tuve, Terr. Mag., vol. 30, p. 15, 1925. Nature, vol. 116, p. 357, Sept. 5, 1925. Phys. Rev., vol. 28, p. 554, September 1926.
[5] Gilliland, B.S.Jour. Research, vol. 6, November 1930. Proc.I.R.E., vol. 19, p. 114, January 1931.
[6] Gilliland, Kenrick, and Norton, B.S.Jour. Research, vol. 7, p. 1083, December 1931. Proc.I.R.E., vol. 20, p. 286, February 1932.
[7] See footnote 3.

taken from the 60-cycle alternating-voltage supply and the pulses were shifted across the screen a known interval of time by means of a phase-shifting bridge similar to that described by Turner and McNamara.[8] The rheostats in the phase-shifting bridge which shifts the phase of the sweep-circuit voltage, were calibrated directly in virtual height, the relation between resistance and virtual height being almost linear. Pulse-retardation time was measured as follows. The ground pulse was centered on the screen by means of an auxiliary bridge, preceding the calibrated bridge. Then the rheostats in the calibrated bridge were adjusted until the pulses corresponding to the various layers were centered on the screen. The corresponding heights were read from the rheostat dial.

In addition to the cathode-ray oscillograph at Sydney, the automatic recording equipment described by Gilliland and Kenrick [9] was used. At Washington a visual recorder with galvanometer oscillograph was used for measuring E-layer critical frequency and also for the measurements at 4,200 kc/s. A manually-operated photographic recorder was used to measure the F_2 critical frequency at Washington.

At Sydney the manual measuring equipment was designed to make a series of critical-frequency determinations of the E-layer, while the continuous recorder was used to make virtual height records at two frequencies which would show changes in the E-layer if its critical frequency decreased. The rest of the apparatus consisted of a portable transmitter and receiver operating with each measuring equipment.

At Washington, three transmitters were located at the Bureau's field station at Beltsville, Md., and two receivers were set up at Kensington, Md. One receiver was alternately tuned to a fixed frequency of 4,200 kc/s and to a series of frequencies near the E critical frequency, while the second was used for F_2-layer critical frequency determinations. The measuring equipment has been described elsewhere.[10] [11] [12]

II. EXPERIMENTAL RESULTS

In order to avoid ambiguity in reference to "critical" frequencies we will discuss them from the point of view of experimental observations.[13] As the frequency is increased through a critical value for the E- or F_1-layer, the ray penetrates the lower layer and is returned from the next higher layer. As the rise takes place, the signals are usually subject to long retardation and high absorption, so that high and rapidly changing virtual heights and small amplitudes are observed through a small range of frequency. The frequency corresponding to the greatest retardation (or sometimes complete absorption) at this virtual height change is interpreted as the critical frequency. The lower limit is the highest frequency at which reflections from the lower layer only are positively returned. The upper limit is the lowest frequency at which reflections from the upper layer are positively returned. These reflections are very much larger than those from the low layer which have a very small amplitude and usually occur above the critical frequency. The critical frequency for the F_2-layer

[8] Turner and McNamara, Proc.I.R.E., vol. 18, p. 1743, 1930.
[9] Gilliland and Kenrick, B.S.Jour. Research, vol. 7, p. 783, November 1931. Proc.I.R.E., vol. 20, p. 540, March 1932.
[10] See footnote 3, p. 830.
[11] See footnote 5, p. 830.
[12] See footnote 6, p. 830.
[13] See footnote 3, p. 830.

is determined in a somewhat different manner. The greatly retarded signals at this critical frequency are often followed by scattered reflections of great virtual height and very small magnitude which have been shown to have no definite relation to the larger F_2-layer reflec-

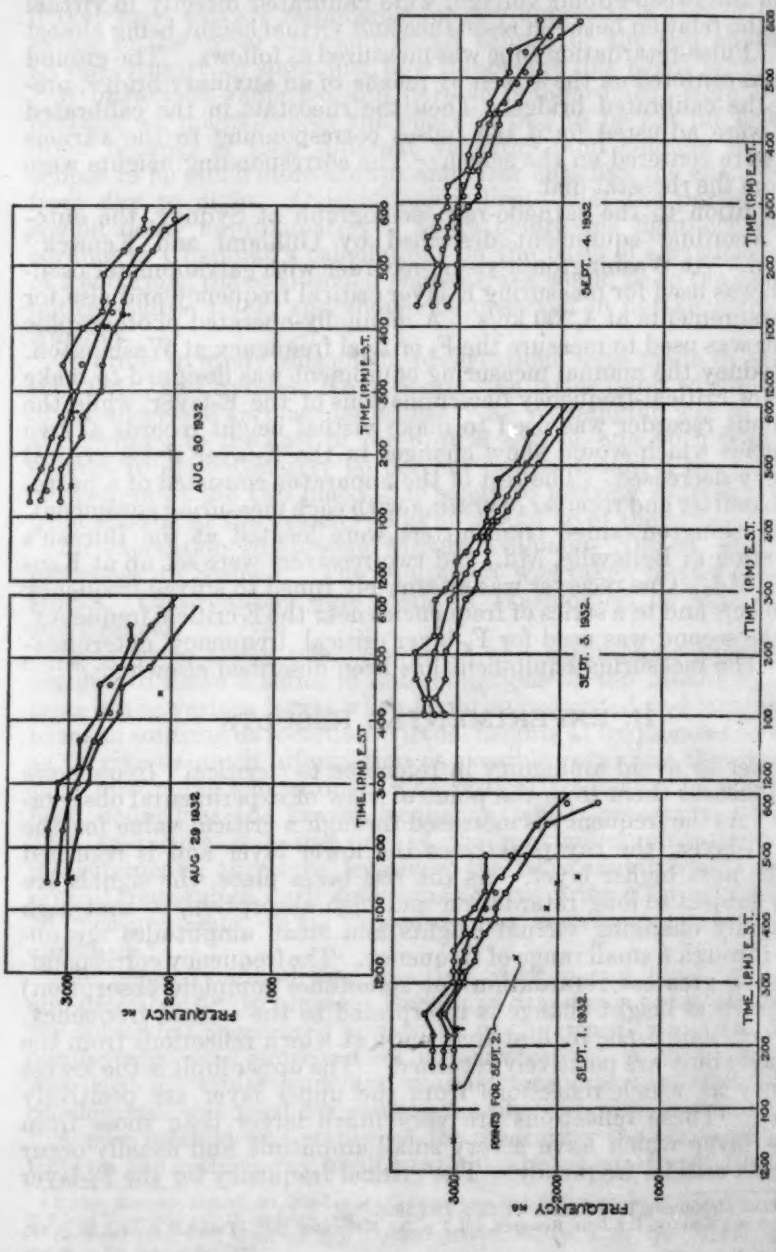

FIGURE 1.—*Variations of f% for days before and after the eclipse. Curves for Washington, D.C., and for Sydney, Nova Scotia, for identical times.*

$f_{\frac{1}{2}}$ at Washington, limiting and mean values.
$f_{\frac{1}{2}}$ at Sydney.

tions. The critical frequency for the F_2-layer is taken as the frequency at which the slope of the frequency-height curve is a maximum, and above which the reflections are not of appreciable magnitude. The lower limit is considered as the beginning of the abrupt rise in the frequency-height curve, and the upper limit is indicated by the positive disappearance of any F_2-layer reflections.

The disappearance of reflections alone is not believed to be always an exact indication of this critical frequency because the high absorption often extending to frequencies well below the critical frequency as defined, would make the results depend somewhat upon the sensitivity of the receiver. The appearance of "scattered reflections" often through an extended range above the critical frequency might also have an influence.

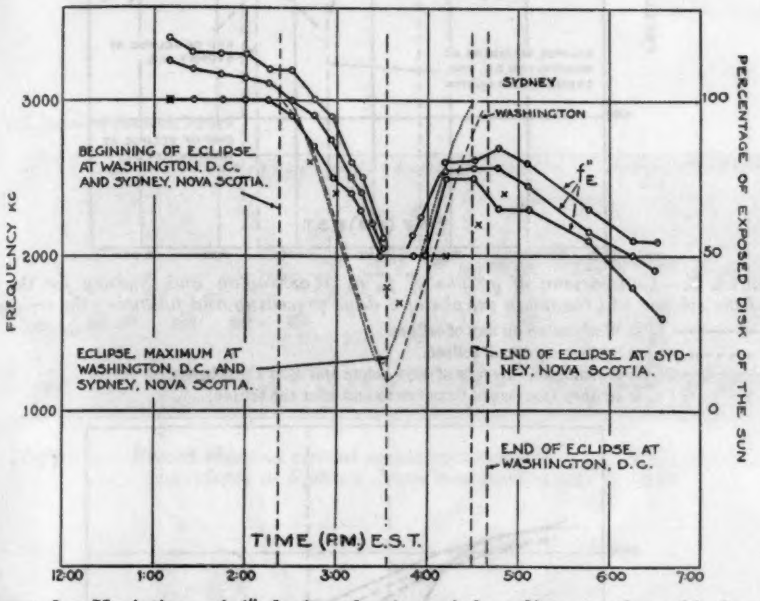

FIGURE 2.—*Variations of f''_E during the time of the eclipse together with the percentage of the exposed area of the sun's disk at Washington, D.C., and Sydney, Nova Scotia.*

—○— f''_E at Washington, limiting and mean values.
× f''_E at Sydney.
– – – Percentage of exposed disk of the sun at Washington.
..... Percentage of exposed disk of the sun at Sydney.

In order to be sure of complete control, observations were made between noon and 6 p.m. on several days before and after the eclipse, as well as on the day of the eclipse. The continuity of these experiments was interrupted only by adjustments of the apparatus and very severe atmospheric disturbances.

III. OBSERVATIONS OF THE E-LAYER

The daily variations of the E-layer critical frequency (f''_E) are shown in figure 1 for days preceding and following the eclipse. Figure 2 shows the variation of f''_E on the day of the eclipse, together

with the percentage of the exposed disk of the sun at Washington and Sydney. The solid line graphs show the values at Washington, while the individual crosses show the values at Sydney for identical times.

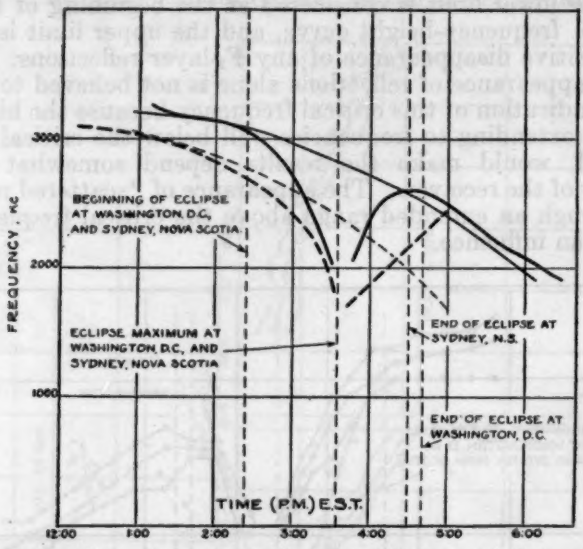

FIGURE 3.—*Comparison of graphs of f''_E at Washington and Sydney for the day of the eclipse and the mean graphs of 6 days preceding and following the eclipse.*

——— f''_E at Washington on day of eclipse.
- - - - - - f''_E at Sydney on day of eclipse.
——— f''_E at Washington (average of days before and after the eclipse).
- - - - - - f''_E at Sydney (average of days before and after the eclipse).

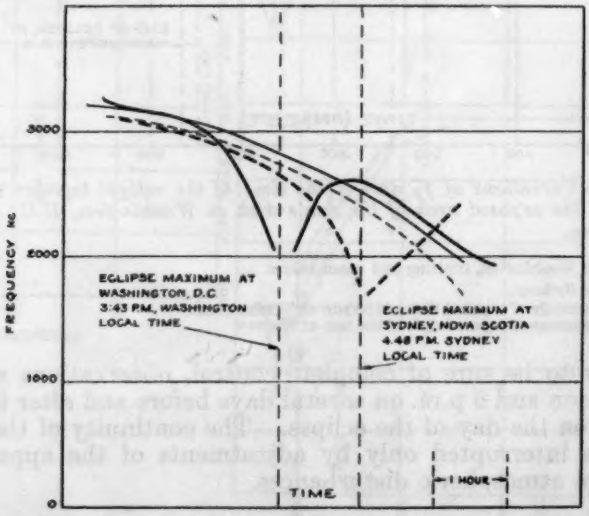

FIGURE 4.—*Same as figure 3 except that the Sydney time is displaced to correct for the difference in longitude of the 2 stations.*

The break in the dip of the f''_E-graph taken at Washington occurred because the rapid change of f_E during this period made accurate determinations impossible. The data show that it is probable

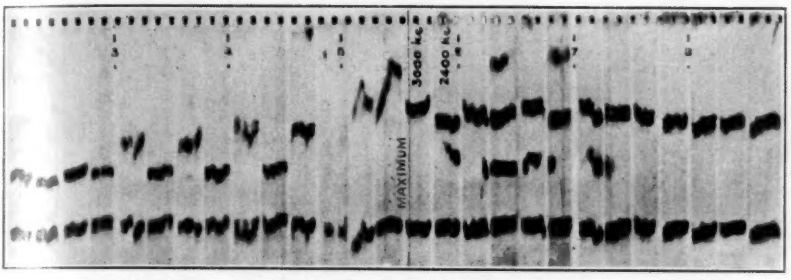

FIGURE 5.—*Record showing virtual height variations of 2,400 and 3,000 kc/s during the eclipse at Sydney, Nova Scotia, August 31, 1932.*

that f''_E did not fall below 1,600 kc/s at Washington. Figure 3 shows the comparison of f''_E for the day of the eclipse and the mean of

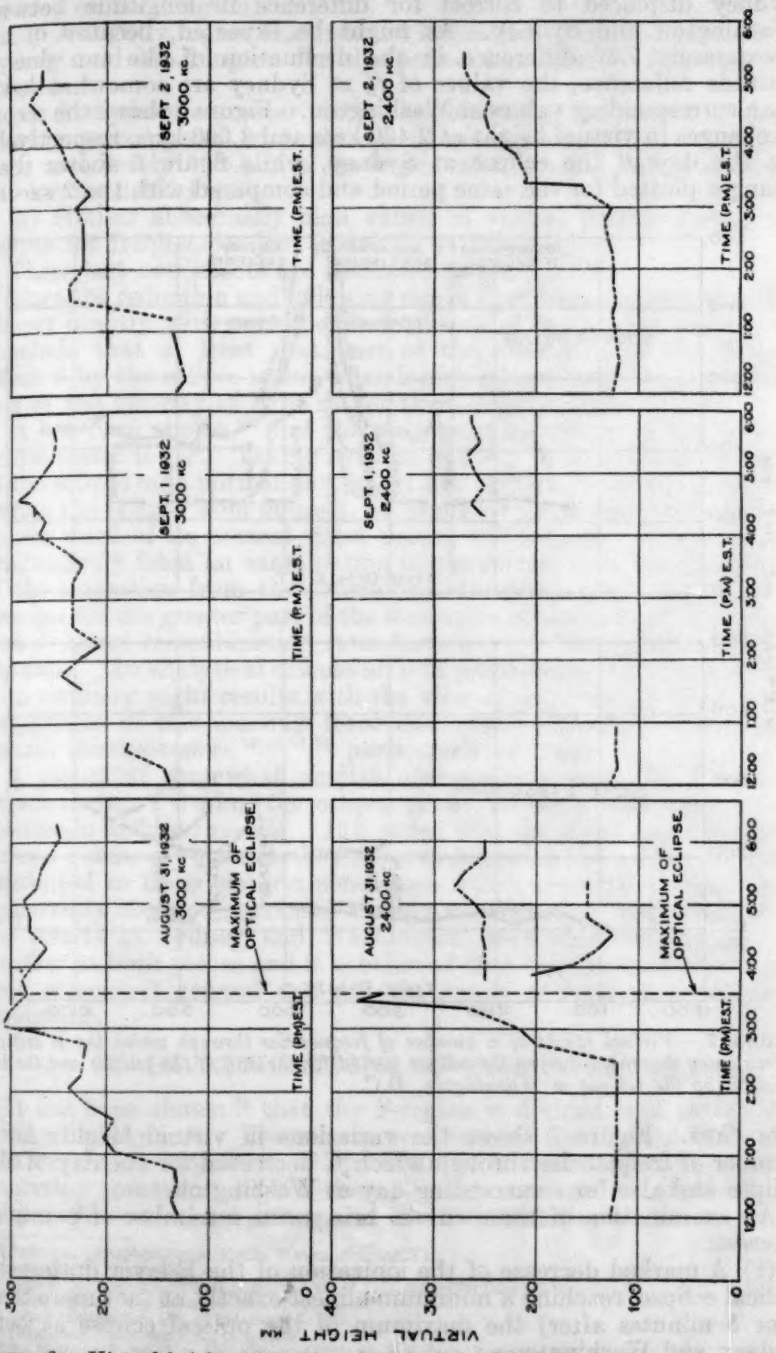

FIGURE 6.—*Virtual heights of 2,400 and 3,000 kc/s plotted for the day of the eclipse and succeeding days at Sydney, Nova Scotia.*

the curves of figure 1 of the 6 days preceding and following the eclipse. Figure 4 shows the same graphs as figure 3 with those for Sydney displaced to correct for difference in longitude between Washington and Sydney. As might be expected, because of approximately 7.3° difference in the declination of the sun due to latitude difference, the values of f''_E at Sydney are somewhat lower than corresponding values at Washington. Figure 5 shows the record of changes in virtual height at 2,400 kc/s and 3,000 kc/s, respectively, for the day of the eclipse at Sydney, while figure 6 shows these changes plotted for the same period and compared with the 2 succes-

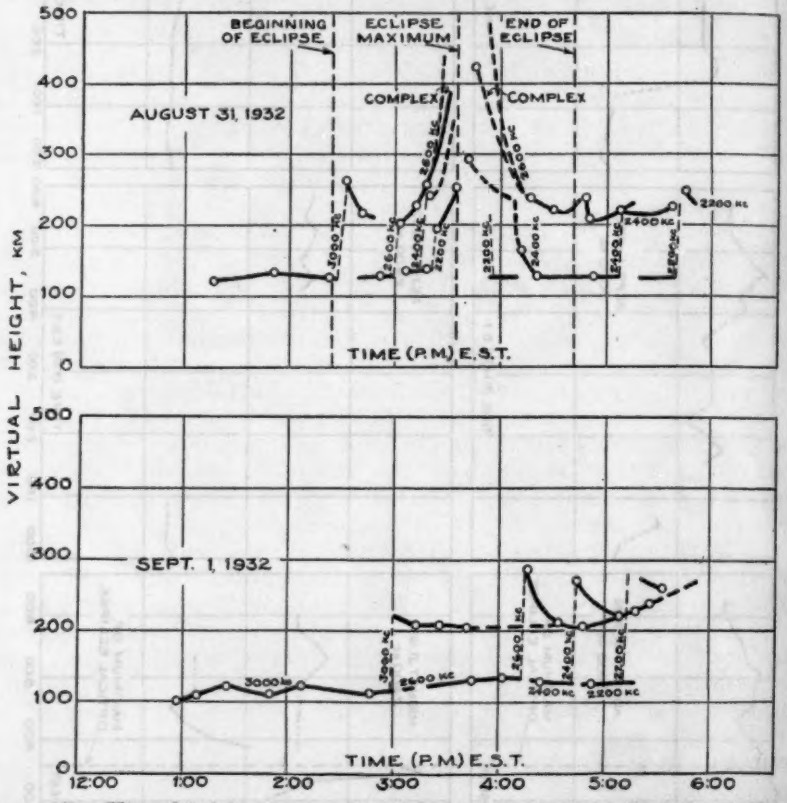

FIGURE 7.—*Virtual height of a number of frequencies through which the E critical frequency decreased during the eclipse period for the day of the eclipse and the day following the eclipse at Washington, D.C.*

sive days. Figure 7 shows the variations in virtual heights for a number of frequencies through which f''_E decreased for the day of the eclipse and also for a succeeding day at Washington.

An examination of these curves brings out a number of points of interest:

(1) A marked decrease of the ionization of the E-layer during the optical eclipse, reaching a minimum almost exactly at (not more than 4 or 5 minutes after) the maximum of the optical eclipse at both Sydney and Washington.

(2) No measurable deviation from the normal value of the ionization of the E-layer for the period just preceding the eclipse at either Sydney or Washington.

(3) A slightly higher than normal ionization of the E-layer at both Sydney and Washington for the period immediately following the eclipse.

(4) At Sydney a greater virtual height during the eclipse of about 280 km as compared with normal values of about 230 km for 3,000 kc/s, and nearly 400 km as compared with normal values of about 220 km for 2,400 kc/s.

(5) Similar abnormally high values of virtual heights during the eclipse for frequencies just above f''_E at Washington.

These last two effects are discussed in section IV.

Since the reduction and following rise in f''_E at both stations coincided almost exactly with corresponding phases of the optical eclipse, we conclude that at least that part of the ionization of the E-layer affected by the eclipse is due to an ionizing force from the sun travelling at the velocity of light rather than to corpuscular effects.

It has been shown [14] that the maximum ionization of the layer is proportional to f''^2_E. Taking a value of 2,850 kc/s for f''_E at the time of the eclipse on a normal day, and 1,650 kc/s for f''_E for the minimum during the eclipse from figure 3, we find that the ionization decreased to one third of its normal value during the eclipse. It can be said qualitatively from an examination of the results that the magnitude of the ionization from the source just described seems adequate to account for the greater part of the ionization of the E-layer in the daytime. Exact recombination rates have not yet been computed from the data. An analytical discussion is in preparation with comparisons with ordinary night results with the view of determining the relative importance of this ionizing force and others known to exist under certain circumstances,[15] [16] [17] [18] particularly at night.

A report of somewhat similar observations made by Canadian experimenters [19] during the eclipse period shows a very close correspondence with our results. It is noted that the slight increase above normal values of f''_E which they observe following the eclipse has been attributed to thunderstorm conditions which occurred at that time. Apparently identical increases already mentioned in connection with the results at Sydney and Washington were observed during fair weather at both places and it is believed that this increase must have been somewhat general and not the result of local meteorological conditions.

IV. INVESTIGATIONS OF THE F_1 LAYER

It has been shown [20] that the F-region is divided into two layers during the daytime. These have been termed the F_1- and F_2-layers. The maximum ionization of the F_1-layer is indicated by a critical frequency somewhat higher than f''_E. At noon on the date of the eclipse, the critical frequency was about 4,200 kc/s.

[14] Pedersen. Propagation of Radio Waves, chapter XI.
[15] See footnote 3, page 830.
[16] Schafer and Goodall, Proc. I.R.E., vol. 20, p. 1131, July 1932 (also 1931).
[17] Gilliland, B.S.Jour.Research, vol. 9, July 1933.
[18] Ranzi, Nature, vol. 130, p. 368, Sept. 3, 1932.
[19] Henderson, Canadian J.R., p. 1, 1933.
[20] See footnotes 3 and 17, p. 830; also see Gilliland, B.S. Jour. Research, vol. 11, p. 561, 1933.

Facilities did not permit a continuous determination of the critical frequency of the F_1-layer. Measurements were therefore made in Washington at a fixed frequency of 4,200 kc/s.

Figure 8 shows the virtual heights for 4,200 kc/s on the days preceding and following the eclipse, and figure 9 shows the virtual heights

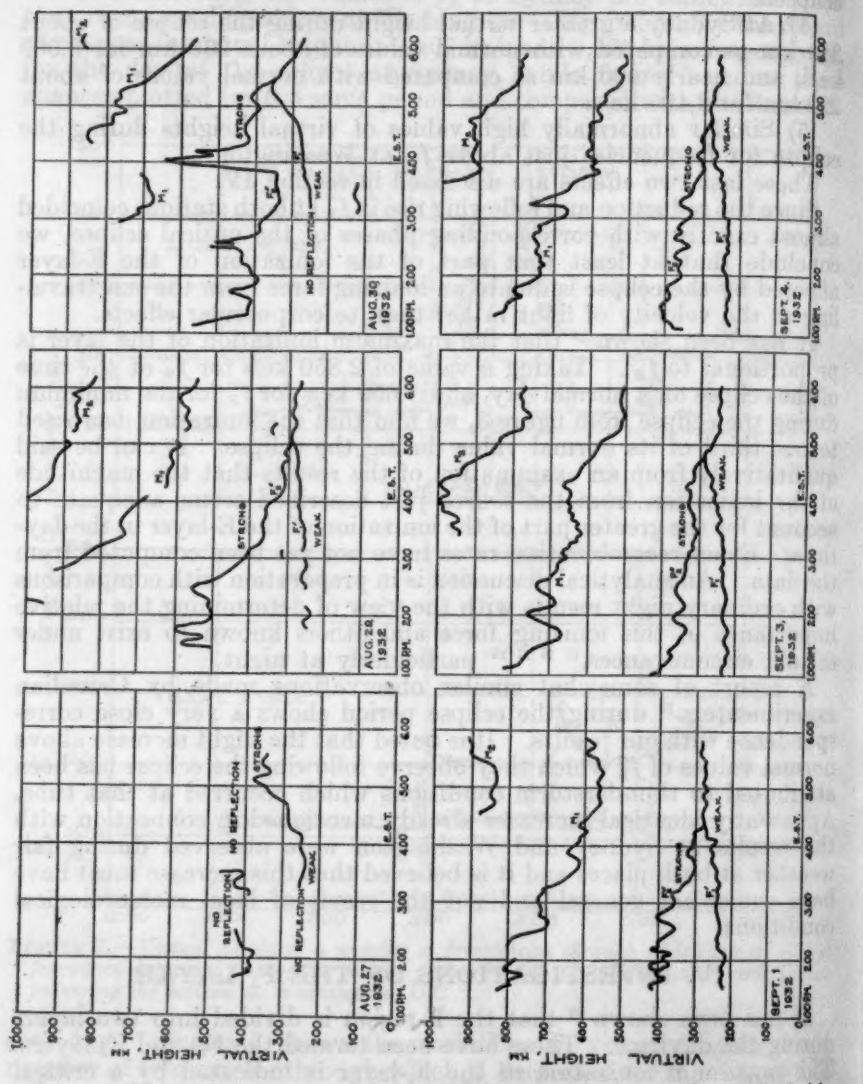

FIGURE 8.—*Virtual heights for a frequency near the noon value of* f''_{F1} *(4,200 kc/s) for days preceding and following the eclipse.*

for this frequency on the day of the eclipse. It has been shown [21] that retardations at this critical frequency for the F_1-layer are frequently subject to a considerable variation during terrestrial magnetic disturbances and therefore the results for August 27, 29, and 30 cannot be considered as representative of normal conditions. Figure

[21] See footnote 3, page 830.

10, therefore, shows figure 9 superimposed on the envelope of the virtual heights for the undisturbed days of September 1, 3, and 4. The variations in virtual height are seen to be quite complex, and the characteristic phenomena associated with the F_1-layer must be taken into consideration in the interpretation of the results.

It has been suggested that the maximum ionization of this layer may be manifest by two critical frequencies because of magnetic double refraction. If we let f''_{F1} denote the ordinary critical frequency and f'_{F1} the extraordinary critical frequency, then $f''^2_{F1} = f'_{F1}(f'_{F1} - f_h)$,[22] [23] where $f_h = 1{,}450$ kc/s.[24] Effects have been observed which appear to confirm this result.[25] At the first critical frequency, therefore, the reflection would consist of two components, reflected

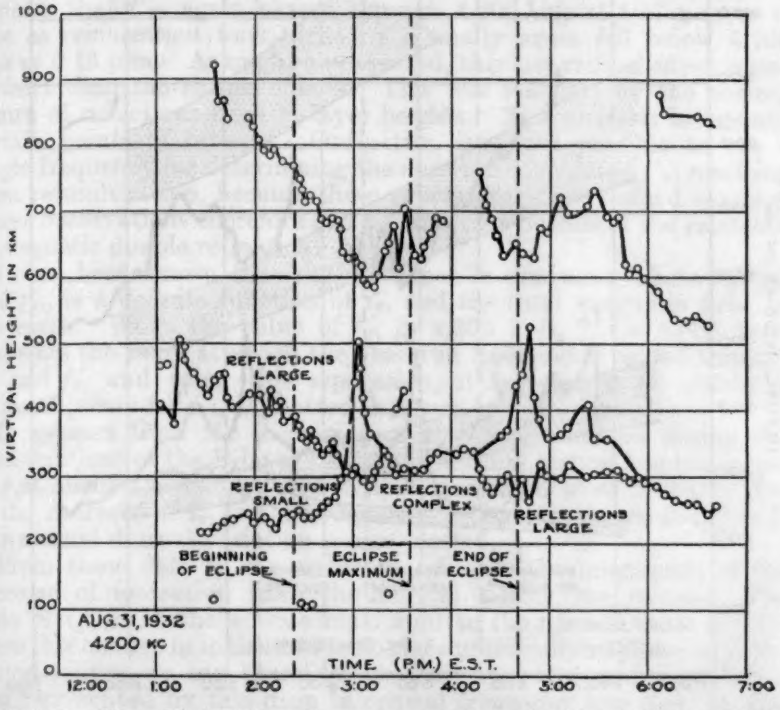

FIGURE 9.—*Virtual heights for a frequency near the noon value of* f''_{F1} *(4,200 kc/s) for the day of the eclipse.*

from different parts of the F-region. The component for which the lesser reduction in refractive index occurs has been termed the ordinary ray designated here as F''_1, having a critical frequency of f''_{F1}. At a frequency just above f''_{F1}, this ray will be reflected from the F_2-layer, but will be subject to a retardation in the F_1-layer and is then termed F''_2. The component for which the greater reduction in refractive index occurs has been termed the extraordinary ray designated here as F'_1 and having a critical frequency of f'_{F1}. It can be shown that the component for which the greater reduction in refractive

[22] See footnote 3, p. 830.
[23] Appleton & Builder, Proc. Phys. Soc., vol. 45, part 2, no. 247, p. 208, March 1933.
[24] This frequency has been determined by assuming a value of 0.52 gauss for the total earth' magnetic field at a height of 180 km at Washington.
[25] See footnotes 3, p. 830; 20, p. 837, and 23.

index occurs (F'_1) will be subject to the greater absorption, at a given frequency.[26]

Referring to figure 8, it is seen that on normal days two components are present. At noon at this frequency the amplitude of the upper reflection is about 1,000 times as large as the lower reflection. It is probable that these two components are due to the double refraction effects just discussed. It is seen that 4,200 kc/s will lie between f''_{F1} and f'_{F1} during the course of the afternoon. In this case the upper reflection at noon is the ordinary ray reflected from the F_2-layer, and suffering long retardation due to its proximity to f''_{F1}. The lower reflection is the extraordinary ray, F'_1. It has been shown[27]

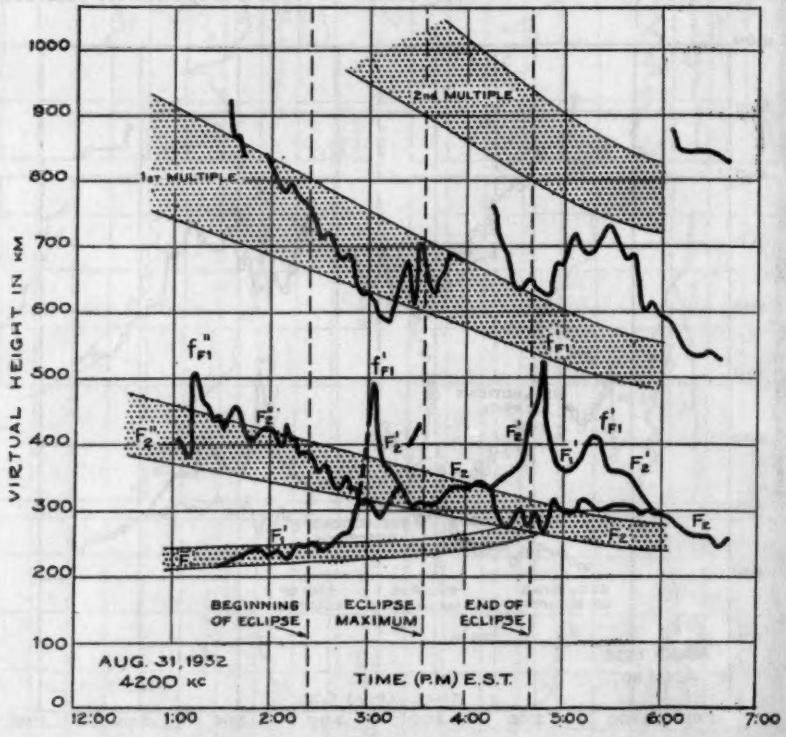

FIGURE 10.—*Virtual heights for a frequency near the noon value f''_{F1} (4,200 kc/s) for the day of the eclipse superimposed on the envelope of the virtual heights for the undisturbed days following the eclipse.*

that for magnetically undisturbed days the upper reflection will generally fall in height during the afternoon for two reasons: (1) The decrease in f''_{F1}, and (2) the decrease in long retardation at f''_{F1}. At the same time, the virtual height for the extraordinary ray is seen to rise because of the decrease of f'_{F1} toward the recorded frequency until the reflected ray joins the F_2 reflection. It is known that the long retardations at f''_{F1} and f'_{F1} are not so great as the afternoon progresses, disappearing in the evening. This effect probably accounts for the fact that on the normal days long retardations

[26] See footnote 23, p. 839.
[27] See footnote 3, p. 830.

accompaning the critical frequency of the second component (F'_1) are not observed on 4,200 kc/s as recombination progresses.

During the day of the eclipse somewhat different effects were observed as illustrated in figure 9. It seems that the rapid decrease in virtual height of the upper reflection after the commencement of the eclipse must have been due to a rapid decrease in f''_{F1}. At the same time, since there was a corresponding decrease of f'_{F1}, the lower reflection rose rapidly in virtual height and appeared to cross the other reflection, reaching a critical value at 3:03 p.m. It appears that 4,200 kc/s becomes the critical frequency at this time for the "extraordinary" (F'_1) ray. The virtual height for this ray then fell, joining the other which was then returned from somewhat high F_2 virtual heights. At 4:17 p.m., the reflections again split and it appears that f'_{F1} again passed through 4,200 kc/s at 4:47 p.m. as it rose as reionization took place. f'_{F1} finally again fell below 4,200 kc/s at 5:13 p.m. As might be expected, this last critical effect is less distinct than the earlier effects. This was followed by the normal return of reflections from F_2-layer heights. This analysis brings out certain points of interest. Ordinarily, it is not possible to use a single frequency for determining the decrease of f''_{F1} and f'_{F1} resulting from recombination, because these effects disappear toward evening. These observations therefore add confirming evidence of the existence of magnetic double refraction.

It has been shown that the difference in frequency between f''_{F1} and f'_{F1}, is a definite function of f''_{F1} and the total magnetic field of the earth. When the value of f'_{F1} is 4,200 kc/s, f''_{F1} is 3,405 kc/s. Knowing the times at which the observed frequencies passed through f''_{F1} and f'_{F1} and using this separation, it is possible to obtain a series of points for f''_{F1}, as plotted in figure 11.

It appears from the discussion of the data obtained during the investigations of the E-layer that the abnormal virtual heights occurring at about 2,500 kc/s at the eclipse maximum were probably due to the decrease of f''_{F1} to this frequency. This was shown in figure 7. The normal diurnal variation is also plotted.

From these data it is possible to estimate the magnitude of the decrease of ionization from the normal during the eclipse. The ratio of $(f''_{F1})^2$ at the eclipse maximum to the normal value is 0.40. Since this change in ionization took place practically in phase with the optical eclipse, we can therefore conclude that the portion of ionization represented by this drop in critical frequency was due, in this layer also, to an ionizing agency traveling from the sun at the velocity of light.

At Sydney, f''_{F1} was determined directly from the automatic records as shown in figures 5 and 6. These points seem reasonably consistent with the Washington data when it is considered that the eclipse occurred a few minutes earlier at Sydney.

The published reports of a number of observers [28 29 30] have been examined and it seems that the variation of virtual heights at frequencies through which f''_{F1} and f'_{F1} decrease can be interpreted in the same manner. From these data, a number of additional points are available, and are shown in figure 11. The variation of the points from

[28] Kenrick and Pickard, Proc.I.R.E., vol. 21, p. 546, April 1933.
[29] Mimno & Wang, Proc.I.R.E., vol. 21, p. 529, April 1933.
[30] Henderson, Can. Jour. Research, vol. 8, p. 1, January 1933.

the dotted curve is to be expected from the differences in latitude and percent totality. It is striking that these points of various observers follow so closely the variation of ionization shown by this interpretation. The interpretation of these effects in terms of a corpuscular eclipse as suggested by Mimno and Wang does not seem to be necessary.

It is of particular interest that the retardations at f'_{F1} remained long until very late in the afternoon. It has been mentioned that the usual disappearance of these effects from the F_1-layer during the afternoon might be due to an actual shifting of the layer. It is evident from the data obtained after the eclipse that the usual cause

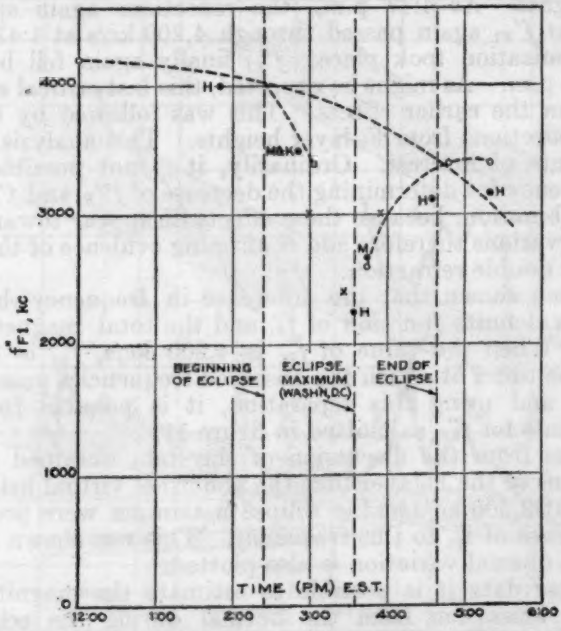

FIGURE 11.—*Variation of f''_{F1} for a normal day compared with that for the day of the eclipse including data plotted from the obervations of other investigators.*

Unlabeled circles indicate Washington measurements. Points marked X indicate Sydney measurements. Circles marked H from Henderson. Circles marked M from Mimno and Wang. Circle marked K from Kenrick & Pickard.

for disappearance of these effects was not present during the eclipse. As a result, the physical aspects of the F_1-layer appear to be about the same as during the early afternoon but with lower ionizations.

V. OBSERVATIONS OF THE F_2-LAYER

Figure 12 shows the F_2 critical frequency (f_{F2}) plotted with known limits for a number of days preceding and following the eclipse. Figure 13 shows the same data for the day of the eclipse, while figure 14 shows the comparison of the eclipse and "normal" data. It should be noted that because we are not certain whether this critical frequency is for the ordinary or extraordinary ray, no distinction in notations is made.

It will be seen that f_{F2} during the eclipse period cannot be said definitely to have undergone any marked change. A decrease of f_{F2} took place during the last phase of the eclipse, but decreases of the same order are found to occur on "normal" days, notably September 1, during about the same time. The values of f_{F2} for August 27 and August 30 are, respectively, just below and just above the values of f_{F2} for the eclipse day during this time. It must be recognized that these latter 2 days were magnetically disturbed, and though no direct correlation has been established between changes at f_{F2} and such

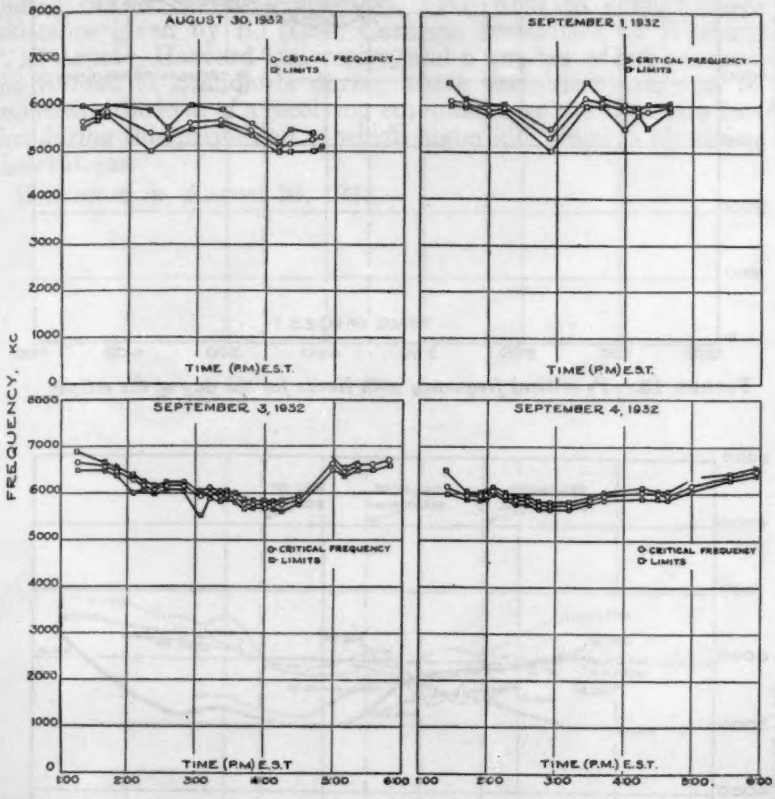

FIGURE 12.—*F_2 critical frequency with limits for a number of days preceding and following the eclipse.*

disturbances, it is possible that they may effect the results during these periods.

It appears, therefore, that no positive results on this can be stated. It can be said, generally, that any changes in f_{F2} which might have been due to the eclipse were not large in magnitude, and were very small compared with the very large changes in f_{F1} and f''_E.

It has been shown by Kirby, Berkner, and Stuart [31] that f_{F2} does not follow the normal characteristics of the lower layers. The possibility that this critical frequency does not indicate a maximum ionization has been discussed, and it has been suggested that the

[31] See footnote 3, p. 830.

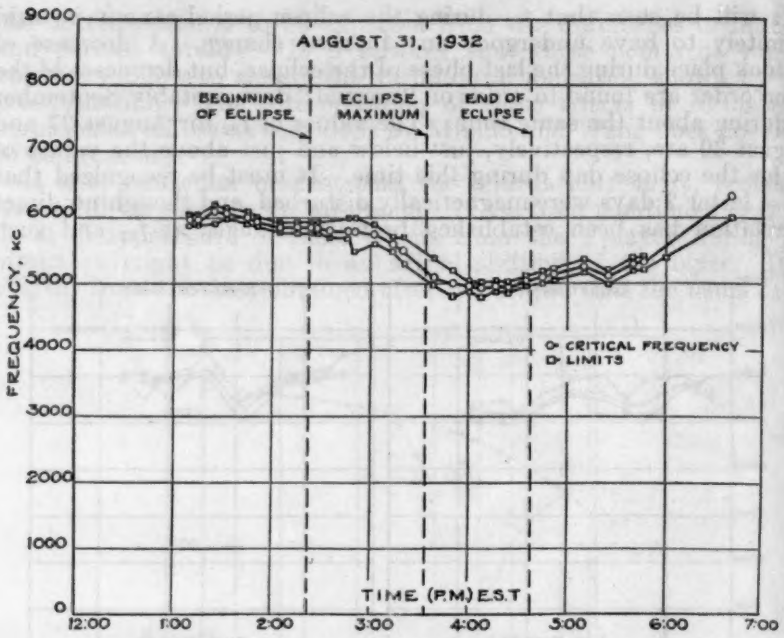

FIGURE 13.—*F_2 critical frequency with limits for the day of the eclipse.*

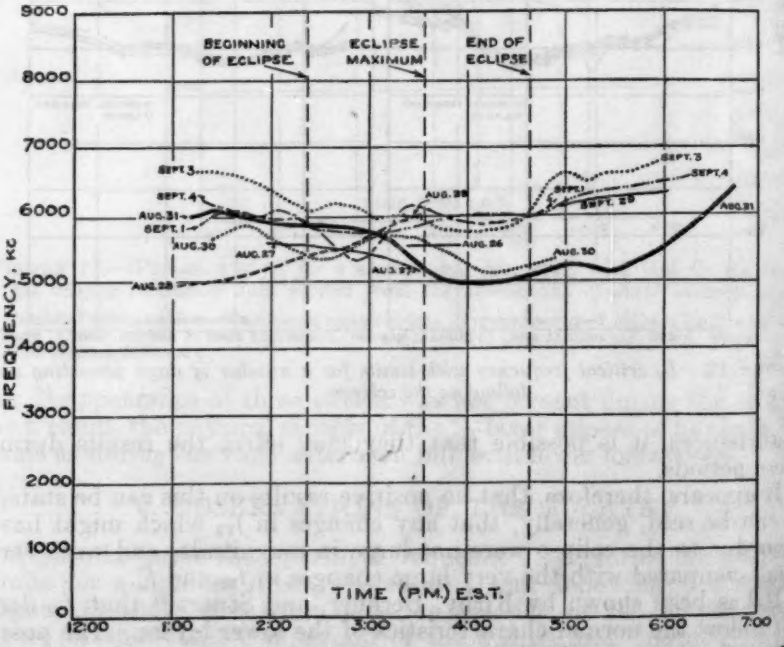

FIGURE 14.—*F_2 critical frequency for the day of the eclipse superimposed on the curves of previous and succeeding days.*

determining factor is absorption rather than ionization. It appears that the observed facts can be explained on this basis. It is possible that recombination occurred in the F_2-layer in the same manner as in the lower layers, but that such changes did not directly affect f_{F2}. From this point of view, the results obtained appear reasonable.

VI. ACKNOWLEDGMENTS

Operations at Sydney were made possible by courtesy of the Canadian Government. The arrangements were made through the United States State Department. We wish to acknowledge the assistance given by B. Haas, Carnegie Institution of Washington; P. N. Arnold, Harvard University, and a number of our associates in the Bureau of Standards during these measurements, and to acknowledge the loan of a receiving equipment by the Carnegie Institution during this period, all of which materially aided in obtaining the observations.

WASHINGTON, August 26, 1933.

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